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GEOCHEMISTRY

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PREFACE

THE geochemical knowledge of today is in a state of vigorous expansion. When we started the preparation of this book two years ago, we planned to give a survey of the field of geochemistry along the lines previously established by one of us (Th. G. S.) in a book published in the Finnish language. However, we soon realized that we had a new book in the making, inasmuch as it was necessary to emphasize the quantitative aspects in geochemistry and to synthesize and summarize the multitude of new ideas and data which had accumulated during the last decade. Therefore, this book has grown far beyond its initially intended scope.

The purpose of this book is neither to serve as a textbook of geochemistry nor to give a complete account of all geochemical information. It is an attempt to survey the broad field of geochemistry and to account for the present state of geochemical knowledge and is mainly intended for the use of the geologist who has the necessary background in chemistry and of the chemist who possesses an adequate knowledge of the geological sciences.

Geochemical research at present is very extensive, and consequently we have made no attempt to stay abreast of the very latest published information. With few exceptions, only papers published up to the early part of 1948 were considered. Furthermore, we did not especially try to cover papers written in other languages than in English, French, and German, because in our opinion such papers generally are not addressed to the international reader.

With respect to errors, omissions, and presentation of data colored by our personal opinions, we wish to quote a word of Goethe:

*Warum ich zuletzt am liebsten mit der Natur
verkehre, ist, weil sie immer recht hat und der
Irrtum bloss auf meiner Seite sein kann.*

KALERVO RANKAMA
TH. G. SAHAMA

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Journal of the American Chemical Society and Dr. W. H. Zachariasen (Fig. 5.13); Cambridge University Press (Fig. 8.6 and parts of Table 6.17); Chemical Publishing Co., Inc. (Table 6.12); Cornell University Press (Figs. 5.5, 5.7, and 5.8); Interscience Publishers, Inc. (equations on p. 336); Wilhelm Knapp, Verlagsbuchhandlung (part of Table 8.10); McGraw-Hill Book Company, Inc. (Tables 5.32 and 8.2, and parts of Tables 5.30 and 7.1); Prentice-Hall, Inc. (Tables 6.16 and 8.13, and parts of Tables 6.7 and 6.17); and The Williams & Wilkins Company (Figs. 8.3 and 8.5).

K. R.
TH. G. S.

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WHAT IS GEOCHEMISTRY?

ONE of the most characteristic features of the modern advances in physics, chemistry, and geology is the ever increasing interest in the boundary zones between these sciences and in the various groups of phenomena within a single science. This development is the consequence of the growing knowledge of natural phenomena and their fundamental essence, and it has given rise to a number of more or less narrowly limited branches of the sciences, represented by their own special methods and problems. At a certain stage of development these branches receive special names corresponding to their programs. Although the border lines between sciences have no very close correspondence in Nature, being only artificially set up by man, they are important in scientific practice. By the use of these boundaries, the natural phenomena are readily divided into groups, and a better view of the classification of sciences and of human research in general is obtained.

Being an offspring of geology and chemistry, geochemistry serves as a mediator between its parent-sciences, collecting its fundamental facts from them and applying the information thus obtained to a better understanding of the chemical phenomena taking place in Nature. Fifteen or twenty years ago geochemistry was still studied by only a few specialists. However, geochemical research has grown extremely rapidly during the last twenty years because it was shown to have important practical applications and unusually many unexplored possibilities of development. Accordingly, the use of the terms geochemistry and geochemical process has grown to be more common than it was earlier. In spite of the development referred to above, these designations, as used today by various authors, are still rather hazy and heterogeneous and have not reached any final uniformity.

Four definitions of geochemistry, differing from one another in point of principle, are presented in literature. F. W. Clarke in his classical book *The Data of Geochemistry* (1924) defines the aims of geochemistry as follows:

Each rock may be regarded, for present purposes, as a chemical system, in which, by various agencies, chemical changes can be brought about. Every such change implies a disturbance of equilibrium, with the ultimate formation of a new

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system, which, under the new conditions, is itself stable in turn. The study of these changes is the province of geochemistry. To determine what changes are possible, how and when they occur, to observe the phenomena which attend them, and to note their final results are the functions of the geochemist.

According to Clarke, geochemistry thus includes all that is chemical in geology. Consequently, the metamorphic changes of rocks where chemical reactions take place, the mineral-facies principle developed by Pentti Eskola, the differentiation of magmas by crystallization, and the granitization phenomena, among many others, should be included in geochemistry proper.

Of course, the actual meaning of the term geochemistry is in itself no natural law formulated on the basis of scientific experience like, e.g., the law of rational indices of crystal faces. Consequently, the above definition does not stand or fall together with a certain opinion, right or wrong, upon which Nature has to pass her judgment. The content and the limits of this branch of science are not defined by Nature herself but by the scientist who tries to make the definition as practical as possible. Accordingly, no one has the right to claim that the meaning put forward by Clarke is completely wrong. One deals simply with a question of adapting the definition to the general scientific nomenclature.

However, there is one thing in Clarke's definition which makes it impossible for us to agree with him or with others following his interpretation. In order to make this point clear, we shall briefly discuss the very precise treatment presented by M. King Hubbert (1938) on the general principles of classification of the sciences.

Hubbert points out that all sciences ultimately deal with identical subjects, viz., with the movements and changing configurations of matter and with the accompanying transformations of energy. Differing from one another only by the subject and/or the scale of treatment, major sciences depend clearly on one another, to the extent that a less fundamental science needs the methods and data of a more fundamental one.

The most fundamental of the sciences is physics, which does not need help from any other science. Therefore, physics belongs to the zero order of dependence. The two major sciences of order 1, viz., chemistry and astronomy, work on an atomic and molecular and on a celestial scale, respectively, and are based on physics. In other words, when chemistry and astronomy leave the elementary stage of purely descriptive treatment, the explanation of observations and

facts is possible only if physical laws and principles are taken into account. The boundaries between physics and chemistry and between physics and astronomy are not sharp, but gradual. Physical chemistry and astrophysics serve as mediators between the sciences of orders 0 and 1.

Geology, which is a science of order 2, differs from astronomy only in the scale of its subject of study, which is the Earth. Geology also depends on physics, as chemistry and astronomy do. Geochemistry and geophysics here play the role of mediators. As to geochemistry, it may, perhaps, be necessary for everything between chemistry and geology to be designated by this name and consequently for the definition given by Clarke to be accepted.

An example is cited from the nomenclature of minerals and of their isomorphic mixtures to illustrate the point. The gradual change from chemistry to geology may be compared with an isomorphic series between two minerals. In such a series between these two "end-member" sciences the various domains included must be arranged by such means that, starting from chemistry, the immediate share of the ways of working and thinking characterizing the chemist decreases, while those peculiar to the geologist increase. The series of the borderland sciences between chemistry and geology may be compared, for example, with the series between albite and anorthite. If the principle of including in geochemistry everything between chemistry and geology is applied, as such, to the plagioclase feldspars, only the name "plagioclase" should be used in petrology for all these mixtures. However, it is apparently more suitable to divide the plagioclase series into separate ranges according to the Ab/An ratio and to give the feldspars falling into these ranges proper names: oligoclase, andesine, labradorite, and bytownite. The boundaries between these subdivisions are artificial because they are set up by the mineralogist and not by Nature herself.

In accordance with the nomenclature of the plagioclase feldspars, it seems suitable to distinguish between the various domains in the borderland between chemistry and geology (Fig. 1). Beginning with geology proper, one comes to chemical geology as the first field. Certainly, it is merely a matter of taste whether or not chemical geology should be included in geology proper. However, the fact cannot be denied that the problems belonging to chemical mineralogy, chemical petrology, and chemical geology represent the first

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stage in the passage from geology to chemistry. These fields of study are included in the definition of geochemistry as given by Clarke, but some authorities disagree with him in this respect. In the Introduction to his book *La Géochimie* (1924), V. I. Vernadsky defines geochemistry as follows:

La géochimie étudie les éléments chimiques dans l'écorce terrestre et autant qu'il est possible dans le globe terrestre. Elle étudie leur histoire, leur distribution dans le temps et l'espace. Elle se distingue nettement de la minéralogie qui n'étudie que l'histoire dans le même espace et le même temps de leur combinaison, cristaux et molécules.

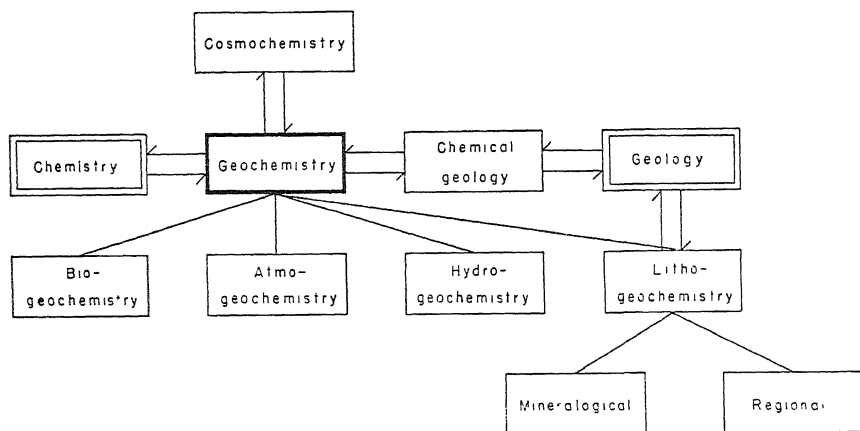


FIG. 1.—Geochemistry and related fields of science

According to Vernadsky, geochemistry and mineralogy are distinguished from each other by the choice of the subject of study.

The subject of study, of course, may be used as a basis when defining a science. However, the geochemist, without moving aside from his field, may sometimes investigate a certain mineral, its chemical composition, its crystal structure, and its manner of occurrence, in order to find the explanation of certain observations concerning the geochemistry of one of its constituents. For example, if the geochemistry of zirconium in igneous rocks is studied, the mineral zircon must be a subject of research. The bulk of zirconium in igneous rocks occurs in zircon, and the peculiarities of the structure of this mineral are apparently responsible for the distribution of zirconium in the various products of magmatic differentiation.

The definition of Vernadsky cited above differs from that given by Clarke by excluding from geochemistry the chemical features of

geology. Hence it cannot be considered exact enough for our purposes.

Another definition of the scope of geochemistry was offered by A. E. Fersman in his book on the geochemistry of Russia, published in 1922. His definition, translated by Tomkeieff (1944), is the following:

The purpose of geochemistry is the study of the element-atom in the conditions prevailing in the Earth's crust (as well as in the parts of the Cosmos accessible to our exact observations). Geochemistry studies: (a) the quantitative distribution of the chemical elements in the Earth's crust and their dispersion and local concentration; (b) the combinations of different elements in the different parts of the Earth's crust and their distribution in space and time under the influence of different chemical processes; (c) the migration of elements and the laws of such migration as determined by the different thermodynamic conditions of their environment; and (d) the behavior of chemical elements either in the environment of the Earth's crust or as compounds and particularly as crystals. This may be expressed even more simply: geochemistry studies the history of chemical elements in the Earth's crust and their behavior under different thermodynamic and physico-chemical natural conditions.

Fersman's definition is rather satisfactory; but the most precise definition of geochemistry is that given by V. M. Goldschmidt on various occasions, e.g., in his classical papers, "Geochemische Verteilungsgesetze der Elemente, I-IX" (1923-37) and "Grundlagen der quantitativen Geochemie" (1933*a*, 1935). Goldschmidt formulates the following three tasks of geochemistry:

1. To establish the abundance relationships of elements and nuclides in the Earth
2. To account for the distribution of elements in the geochemical spheres of the Earth, e.g., in the minerals and rocks of the lithosphere and in natural products of various kind
3. To detect the laws governing the abundance relationships and the distribution of the elements

It is evident that the definitions given by Vernadsky, Fersman, and Goldschmidt are of identical meaning, although the expression used by Goldschmidt is by far the most precise. Therefore, his definition will be followed in this book. Our leading principle when defining geochemistry is not the subject of study but the viewpoint of the scientist attacking his problems. The geochemist deals largely with geological phenomena and geological subjects. His entire work is based on chemistry. His methods and, as may be especially emphasized, his problems are those of a chemist or a physical chemist.

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This very fact enables one to draw the boundary line between geochemistry and chemical geology. Conversely, the chemical geologist examines his problems from the viewpoint of a geologist. His is a geological material, and, when interpreting his observations, the analytical results, etc., he always has their geological application in his mind. For the geochemist, on the other hand, the geological observations, though based on the use of geological material, represent only a certain part of his results, which are intended to establish laws governing the abundance and distribution of the elements.

If geochemistry is defined in the manner explained above, the drawback included in the definition given by Clarke is avoided, i.e., that the domains of geochemistry and chemical geology overlap to a considerable degree. When defining the borderland fields between the sciences, it is desirable for the new branches to cover continuous series of phenomena without falling into the customary ranges of their neighboring branches.

The principles discussed above, by which geochemistry must be separated from chemical geology, are found in Goldschmidt's definition. We feel, however, that it is necessary to emphasize the decisive importance of the point of view of the scientist when judging whether or not a given problem belongs to geochemistry. In order further to illustrate this fact, the following example is cited.

It is supposed that both the geochemist and the geologist (or the petrologist) deal with the differentiation by crystallization of a magma. The question is: How do their attitudes toward this problem differ from each other? The two scientists need a thorough knowledge of the mechanism of the differentiation process as a whole. The petrologist tries to reveal the succession of the various products of differentiation and the causes responsible for this sequence. In his case the field observations, supported by laboratory experiments, which justify a certain succession of rocks, represent the final result of the process. In field work he will apply the results to the special problems of his region. In the case of the geochemist, on the other hand, the succession of the rocks as established during field and laboratory observations represents no final result of the research but merely forms a basis for the determination of the degree of enrichment of the various elements in the products of differentiation. The scope of his work is to find out the properties of the elements or of their ions which are responsible for the enrichment phenomena observed.

WHAT IS GEOCHEMISTRY?

According to the definition adopted in this book, geochemistry may be divided into four branches, devoted to more restricted fields, i.e., the four geochemical spheres. The division is schematically presented in Figure 1. It might be pointed out that Vernadsky was the first to use the name biogeochemistry. A very definite regional trend is developing in the geochemical investigation of the lithosphere—lithogeochemistry—contrasting with the trend which may be called classical or mineralogical. Although geology, as one of the parental sciences of geochemistry, furnishes most of the material used by the latter, the value of other sciences cannot be denied. Biological material and the results of biochemical research form the background of biogeochemistry. The knowledge of the geochemistry of the atmosphere is based nearly exclusively on meteorological research. Much information on the chemical composition and physical condition of the seas, which is of fundamental value in the study of the geochemistry of the hydrosphere, is collected in oceanographical investigations.

HISTORICAL OUTLINE

GEOCHEMISTRY, as an independent field of study, is not very old if compared with its parent-sciences, geology and chemistry. The name geochemistry was used for the first time in 1838 by the Swiss chemist, Christian Friedrich Schönbein (1799–1868), the discoverer of ozone. He (1838) mapped out the program for the new branch of science and emphasized the importance of studying in the greatest detail the properties of all geological formations, their physical and chemical properties, and their age relationships. He also stressed the importance of carefully comparing the products of the chemical forces active at the present with those of earlier forces. In 1842 he again emphasized the significance of geochemistry, stating that for real geological research the chemical nature and the manner of origin of the masses constituting the Earth were of an importance at least equal to that of the age of the geological formations and the fossil remains of plants and animals imbedded therein.

Studies of a geochemical character had already been made prior to Schönbein's time, during the period of the growth and development of mineral chemistry, which certainly is the most orthodox inorganic chemistry. The name of the Swedish chemist, J. J. Berzelius (1779–1848), must be mentioned in this connection. However, the most part of the geochemistry of the past was mineralogical and geological chemistry, dealing with the study of mineralogy and geology, with special reference to the chemical reactions involved.

More extensive discussions dealing with the field and problems of geochemistry were given by some of Schönbein's contemporaries in Germany. In the middle of the nineteenth century Gustav Bischof (1792–1870) discussed these questions in his *Lehrbuch der physikalischen und chemischen Geologie*, the first edition of which was published in 1847–54. Toward the end of the century (1879–93) Justus Roth (1818–92) published a similar treatise, *Allgemeine und chemische Geologie*. The book *Chemische Mineralogie* by Reinhard Brauns (1861–1937), issued in 1896, also contains important earlier contributions related to geochemistry.

The first, and one of the most important, contributions to geo-

chemistry in the modern sense was the classical treatise, *The Data of Geochemistry*, written by the American mineral chemist, Frank Wigglesworth Clarke (1847–1931). The first of the many editions of this book was published in 1908. It is an extensive and systematic collection of facts pertinent to the accessible parts of the Earth. Consequently, Clarke's book today is still one of the most valuable source books of geochemical knowledge.

Henry Stephens Washington (1867–1934), Clarke's contemporary, also made important contributions to the study of the Earth's interior, the composition of the lithosphere, and the abundance of the elements therein.

In Europe many early contributions of importance in the deciphering of the geochemistry of the lithosphere were published around the beginning of the twentieth century. Two Norwegian scientists, J. H. L. Vogt (1858–1932) and W. C. Brøgger (1851–1940), studied the crystallization of igneous rocks, and Vogt also made important earlier contributions to the occurrence and abundance of the less familiar elements in rocks. V. M. Goldschmidt (1888–1947) in Norway studied the physical chemistry of metamorphic rocks. The Swiss petrologist, Paul Niggli, has also contributed to the development of geochemistry.

The Russian school of geochemistry, under the leadership of V. I. Vernadsky (1863–1945) and his younger contemporary, A. E. Fersman (1883–1945), made the first attempts to establish an independent science of geochemistry. In 1924 the former published, in French, his book *La Géochimie* (which was later published in Russian and German), followed, in 1929, by another book, *La Biosphère*. The geochemical study of the biosphere remained among the subjects of main interest to Vernadsky, whereas Fersman focused his activity on the geochemical investigation of the lithosphere, particularly with the help of mineral assemblages and their development into genetic types, with much attention paid to the regional side of such studies. Fersman also sought the ultimate causes of the distribution of the elements in their atomic structure and studied their distribution in the Universe, thus incorporating geochemistry with cosmochemistry. His research resulted in a monumental book of theoretical and applied geochemistry, written in Russian and published in 1933–39, and in extensive studies on the geochemistry of granite pegmatites.

Beginning with the third decade of the twentieth century, a new period of evolution started in geochemistry, which led, in a com-

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paratively short time, to the discovery of the fundamental laws governing the distribution of the elements in Nature. This development in geochemistry was due mainly to the persistent work of V. M. Goldschmidt and his many co-workers at the mineralogical institutes of the universities of Oslo and Göttingen. As a result of this activity, which lasted for nearly two decades, the actual distribution of a great number of elements was established. The new development in geochemistry was partly incorporated with the evolution of modern physics, especially of atomic and nuclear physics, and partly with the development of new physical and chemical methods of quantitative determination of the elements even in very low concentrations, particularly with the aid of optical and X-ray spectrochemical analysis. It must be emphasized, however, that geochemistry, for its part, contributed notably to the evolution of physics and chemistry during this period. Actually, the use of optical spectrochemical analysis dates back to its earliest beginnings in 1860, when the German scientists, Robert Bunsen (1811–99) and Gustav Kirchhoff (1824–87), discovered a new element, cesium, in the water of the Dürkheim mineral springs in Germany. Another new alkali metal, rubidium, was discovered by Bunsen and Kirchhoff in 1861 in lepidolite, also with the aid of spectrum analysis. The Swedish geologist, Assar Hadding, was the first to show, in 1922, that X-ray spectrography is a very useful tool in chemical analysis.

Fundamental research dealing with the distribution and abundance of the elements in Nature was also carried out on an extensive scale, after the first two decades of the twentieth century, by George Hevesy and his co-workers in Denmark and Germany and by Ida and Walter Noddack in Germany.

The various branches of geochemistry are today studied by an increasing number of scientists in the various countries. So far, research in the geochemistry of the lithosphere has been largely concentrated in three Fennoscandian countries: Norway, Sweden, and Finland. Thermochemistry and the use of separated isotopes and artificially radioactive elements are likely to become important new tools in this branch of geochemistry. There is also a definite trend in lithogeochemistry toward the study of geochemical phenomena on a regional, even on a global, scale—the opposite of the classical mineralogical trend in this field. Research in oceanography is largely devoted to the study of many of the fundamental problems in oceanic geochemistry, particularly owing to the development of

HISTORICAL OUTLINE

new sampling equipment for ocean-bottom deposits. One of the more recent tendencies in biogeochemistry deals with the distribution and role of trace elements in plants and animals.

The goal of present research in theoretical geochemistry is the detection of the primary causes of geochemical phenomena and the basis underlying geochemical laws. Much new light is shed on these problems by the evolution of astrophysics. Geochemistry is thereby definitely linked with cosmochemistry.

INTRODUCTION

THE subject matter contained in this book is divided into two parts. Part I deals with the general laws and regularities which determine the abundance and manner of occurrence of each particular element. This way of presenting the material is in accordance with the definition of the three main tasks of geochemistry, discussed on page 5. Part II, on the other hand, deals with the individual geochemical features of each of the elements in the Periodic System, as well as with the empirically established causes of the manner of occurrence of the various elements.

If the general geochemistry of a given element is considered, its terrestrial and cosmic abundance is found to be of fundamental importance. The essential influence of the abundance of an element on its manner of occurrence is understood if the law of mass action is taken into account. This well-known physicochemical law regulates the course of a chemical reaction taking place in the laboratory, and it is evident that it is valid also in the case of such reactions which occur in Nature. However, it must be emphasized at once that there is a fundamental difference between the chemical reactions studied in laboratories and those investigated in Nature. The first category includes those of a limited scale, their course being widely controlled and readily deciphered. These reactions, in addition, sooner or later usually attain equilibrium. The scale of the reactions met in Nature, on the other hand, is immense, and in most cases the reaction equilibrium is never attained or is reached only after long periods of time. Thus only limited parts of the reacting system can be observed, and the details of the mechanism of the reaction usually remain more or less unknown. Consequently, in geochemistry often only the substances originally present or the reaction products are available for study, and the actual course of the reaction must be deduced from analogous evidence furnished by laboratory experiments. As pointed out by Paneth (1940), the geological sciences, which furnish geochemistry with much of the material studied, frequently suffer, in addition, from the peculiar nonmathematical character of their logical structure, whereby their conclusions may appear to many representatives of other sciences less stringent than

they actually are. The result is that much geological knowledge is required of the successful geochemist, along with a thorough understanding of the laws of physical chemistry.

The nature of the products formed in both endogenic and exogenic reactions depends decisively on the concentrations of the participating elements, i.e., their abundance. Although the local concentrations of the reacting compounds in Nature are governed by many factors, they depend ultimately on the abundance relationships of the elements in question. It must be added, on the other hand, that the knowledge of the abundance relationships of the elements still does not suffice to determine quantitatively the nature of the substances formed in the reaction. The rapid increase in understanding of the ultimate composition of the atomic nucleus has resulted in the fact that now the geochemist must also consider the abundance of the nuclides which compose the various elements, in order completely to understand the abundance relationships of the latter.

Consequently, the study of the abundance of the elements and of the nuclides—the first of the main tasks of geochemistry—is one of the more important subjects to be discussed in Part I of this book. It forms the basis of the treatment of the geochemical differentiation of matter, which has caused the present chemical composition of the various geochemical spheres of the Earth and of the Earth itself. The processes involved in the geochemical differentiation of matter are largely theoretical, and many of their details must still be verified by additional facts. However, they are employed in the present treatise because they offer, to the best of our present-day knowledge, a logical chain of events which can be successfully used in geochemical philosophy, i.e., in the construction of a geochemical *Weltbild*. The processes, discussed by Goldschmidt (1926, 1930a, 1933b), include the following:

1. The first geochemical differentiation of matter. This group includes all processes responsible for the differentiation of matter to form the geochemical spheres of which the Earth is now believed to be composed. The concept of the first geochemical differentiation is based on geophysical facts concerning the Earth; physical and chemical facts pertaining to the structure and composition of meteorites and other astrophysical information; and the results obtained from metallurgical studies dealing with the melting and preparation of metals from their ores.

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2. The second geochemical differentiation of matter is called in petrology the differentiation by crystallization of a magma. This process is believed to be the main mechanism in the formation of rocks and minerals from their melts. It requires understanding of the fundamental facts of crystal chemistry, which are presented accordingly.

3. The third geochemical differentiation of matter takes place in the zone of the exogenic phenomena. It deals chiefly with physico-chemical processes in aqueous solutions which result in the formation of the various sediments and sedimentary rocks. The processes involved are therefore discussed.

The major cycle of matter, the metamorphism of rocks connected therewith, and the endogenic migration of matter in the lithosphere differ largely from the three differentiation phenomena discussed above and consequently are treated in separate subdivisions, which deal with their fundamental principles.

The above discussion is focused principally on the lithosphere and its geochemistry. The three outermost geochemical spheres of the Earth, viz., the hydrosphere, the atmosphere, and the biosphere, are also studied as separate geochemical units. Although their masses, as compared with that of the lithosphere, are rather small, they are geochemically rather important and may have decisive influence upon phenomena taking place in the lithosphere.

The field of geochemistry, by its definition, is restricted to the Earth. However, some of the results of geochemistry may be applied to the study of the chemistry of the other members of the Solar System. On the other hand, much information of direct geochemical importance is today obtained from astrophysical studies, and it is evident that geochemistry is but a branch of the general chemistry of the Universe, called cosmochemistry. Therefore, a short account is given of some subjects of cosmochemical importance, such as the chemistry of comets and meteors, internal constitution of the planets, and the chemistry and evolution of their atmospheres.

In accordance with the definition of one of the fundamental tasks of geochemistry, an outline of the geochemical evolution of the Earth is presented, based on the general information available in the preceding chapters.

PART I
GENERAL GEOCHEMISTRY

COMPOSITION AND STRUCTURE OF METEORITES

METEORITICS¹ AND GEOCHEMISTRY

THE meteorites collected all over the world, available for research in the museums and collections of different countries, are often believed to be fragments of a member of the Solar System, scattered in a manner similar to the asteroids (Paneth, 1940). The broken planet must have been comparable to the Earth in size in order to have possessed a metallic core from which the irons were produced. Brown and Patterson (1948) showed that, if the distribution of the elements in meteorites represents an equilibrium, the meteorites had their origin in the interior of a planet similar to the Earth in general physicochemical characteristics. The hypothesis is also generally accepted that the asteroids were derived from this same parent-body.

The meteorites are excellent specimens of matter from space, and they supply information on the properties and composition of matter found outside the Earth. Being the sole representatives so far available of extra-mundane material, they are an extremely important source of the knowledge of interplanetary and interstellar masses. It has been calculated that over half the sporadic meteors come from interstellar space. However, geochemistry is restricted in its field to the Earth, and hence the investigation of meteorites does not exactly fall within its scope. A treatment of the fundamental petrological and chemical properties of meteorites would thus seem to be incorrect as far as a treatise on geochemistry is concerned.

However, the meteorites also have terrestrial importance, since the meteoritic matter contributes to the mass of the Earth with a daily amount of 1 metric ton (Watson, 1941). It is calculated that during

1. The terminology in meteoritics, proposed by Nininger (1936), is used in this book.

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the geological history of the Earth (taken as $2,000 \cdot 10^6$ years) the total accumulation would amount to $10^9 \text{ g} \cdot \text{km}^{-2}$, a layer less than 1 cm thick over the whole surface of the Earth. Other important reasons for the significance of the meteorites in geochemistry are the following:

1. According to the present knowledge, the physical properties of the Earth do not remain unchanged from the surface to the center of the globe but are subject to regular changes, which are discovered by means of various geophysical methods. There is no direct evidence concerning the chemistry of the Earth's interior. The knowledge of the chemical composition of the Earth and of its various geochemical spheres, on the other hand, is the fundamental basis of geochemistry. Because direct observations of the Earth's interior are not possible, the geochemist must draw his conclusions in an indirect manner. In addition to the facts offered by geophysics, the only way of obtaining this information is by analogy with the meteorites. The French geologist, A. Boisse, had already suggested in 1850 that the meteorites formed a counterpart of the interior composition of the Earth. This suggestion is now rather generally accepted, even though the present evidence is still far from complete. Consequently, if any geochemical conclusions are drawn concerning the Earth's interior, the chemical composition of the meteorites must be taken into account. If the composition of the meteorites is wholly ignored, then the only actually existing basis of the research is lost, and the result is pure speculation, of no scientific value whatever. On the other hand, it must also be kept in mind that a strict analogy between the Earth and the meteorites is still by no means a necessity.

2. The manner of occurrence of the elements in the lithosphere and their distribution among the theoretical geochemical shells of the Earth depend on the chemical and geochemical properties of the elements. The distribution of the elements among the various meteorite phases, along with other facts, gives some information concerning their general geochemical character. The case may be illustrated with an example. According to the theory now generally accepted, the Earth has a core consisting of nickel-iron. In the meteorites the rare element germanium is found to be very strongly enriched in the metallic phase, and the distribution ratio between metal and silicate amounts to approximately 99:1. If this result were applied to the Earth, one would expect germanium to be greatly enriched in the metallic core. However, such an analogy between

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the Earth and the meteorites cannot be established. As a matter of fact, certain circumstances, which will be discussed later, prevent a very far-reaching analogy. At any rate, the results concerning the meteorites are often helpful in understanding some peculiarities in the manner of the terrestrial occurrence of the elements.

In accordance with the principle discussed above, no attempt will be made to give an exhaustive review of the knowledge of meteoritics. Only some data will be reported which are considered to be of general importance in the application of the available information concerning meteorites to the discussion presented in the coming chapters of this book.

MINERAL CONSTITUENTS OF METEORITES

The constituents of the meteorites which are called meteorite minerals² are partly identical with those found in terrestrial rocks of a corresponding chemical composition. The meteorite minerals are listed in Table 1.1. Some substances of a dubious character or imperfectly known are not included (see Neuerburg, 1946). Short descriptions follow of the minerals listed in Table 1.1.

Nickel-iron.—The nickel-iron consists of two different meteorite mineral species, kamacite and taenite (see Henderson and Perry, 1943; Perry, 1944). They are nickel-iron alloys which differ from each other in their nickel content and crystal structure. Small amounts of cobalt are always present, playing structurally the same role as nickel. The nickel content of kamacite is rather uniform. It is never higher than about 6 per cent (cobalt included), and only a few recent analyses show nickel contents materially lower than 5 per cent. The structure of kamacite is that of the body-centered isometric α -iron. Taenite is richer in nickel than is kamacite. The content ranges from approximately 13 per cent to as high as perhaps 48 per cent. The composition of taenite is thus rather variable. The question of whether there exists any intermetallic compounds between iron and nickel with fixed ratios of these elements seems thus far not to have been decisively settled. The structure of taenite is that of the face-centered γ -iron. Both kamacite and taenite are isometric. The third variety of the nickel-iron listed in Table 1.1, viz., plessite, is not a definite meteorite mineral, being, instead, a supersaturated solid solution of taenite with respect to kamacite.

2. Because a number of the constituents of the meteorites are not known to occur terrestrially, we propose to use in this book the term meteorite mineral to distinguish between the compounds found in meteorites and the terrestrial minerals.

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Its composition varies according to the relative amounts of these components.

Graphite and diamond.—Graphite is rather common, but the other crystalline form of carbon—diamond—is extremely rare, being reported in only some iron meteorites.

Copper.—Native copper is a very rare constituent of the siderites.

TABLE 1.1*
THE METEORITE MINERALS

ELEMENTS:	OXIDES:
Copper	Magnetite
Nickel-iron	Chromite
<i>Kamacite</i>	Quartz
<i>Taenite</i>	Tridymite
<i>Plessite</i>	
Carbon	CARBONATES:
Diamond	Breunnerite
Graphite	
CARBIDES:	PHOSPHATES:
Cohenite	Apatite
<i>Moissanite</i>	
	SILICATES:
NITRIDES:	Olivine
<i>Osbornite</i>	Clinoenstatite-clinohypersthene
	Diopside-hedenbergite
PHOSPHIDES:	Augite
<i>Schreibersite</i>	Enstatite-hypersthene
	Plagioclase
SULFIDES:	
<i>Troilite</i>	GLASS:
<i>Oldhamite</i>	<i>Maskelynite</i>
<i>Daubréelite</i>	
CHLORIDES:	
<i>Laurencite</i>	

* The species not found in terrestrial rocks are printed in italics.

Cohenite, $(Fe,Ni)_3C$.—Cohenite crystallizes in the orthorhombic system. It corresponds to the artificial iron carbide (cementite) which occurs in steel. Even though nickel does not form a carbide in man-made iron, cohenite contains noticeable amounts of this metal. The average composition of cohenite, which is a rare constituent of the meteorites, is given in Table 1.2, which is quoted from Chirvinsky (1931).

Moissanite, SiC .—Moissanite is hexagonal, identical with the artificial silicon carbide, and very rare.

Osbornite, TiN .—This constituent is isometric and extremely rare.

COMPOSITION AND STRUCTURE OF METEORITES

Schreibersite (rhombite), $(Fe,Ni,Co)_3P$.—Schreibersite is tetragonal. It is very rich in nickel and is one of the most common accessory constituents of meteorites. The average composition of schreibersite is presented in Table 1.2. In some irons it occurs as parallel-oriented lamellar grains (Reichenbach lamellae), resembling in appearance the kamacite plates of the hexahedrites.

Troilite.—This hexagonal meteorite mineral with the composition FeS is very abundant in all types of meteorites and is structurally identical with the terrestrial pyrrhotite (Fe_5S_8 – $Fe_{11}S_{12}$) but shows, contrary to the latter, no excess of sulfur. According to Laves (1930),

TABLE 1.2
AVERAGE CHEMICAL COMPOSITION OF TROILITE,
SCHREIBERSITE, AND COHENITE

ELEMENT	TROILITE	SCHREIBERSITE	COHENITE
	Per Cent		
Fe	62.26	58.33	90.28
Ni	} 1.72	25.85	} 3.46
Co..		0.59	
Cu		0.19	
S..	36.42		
P.		15.18	
C. . .			6.26
Total . . .	100.40	100.14	100.00

the apparent excess of sulfur generally found in pyrrhotite is actually due to the fact that a number of positions of the iron atoms are left vacant in the structure. Vacant positions do not occur in the structure of troilite, and its composition thus corresponds fairly well to the theoretical formula of iron monosulfide, FeS. Small amounts of nickel and cobalt are present, replacing iron. The average composition of troilite is presented in Table 1.2.

Oldhamite, $(Ca,Mn)S$.—Oldhamite is usually considered to be calcium sulfide, CaS; but Goldschmidt (1937*b*) showed that it contains appreciable amounts of manganese. This is due to the fact that manganese sulfide, occurring terrestrially as alabandite (MnS), has the same isometric sodium chloride structure as calcium sulfide. Its structural dimensions are nearly identical with those of CaS, and consequently it is isomorphic with the latter. Oldhamite also

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contains magnesium along with manganese. It is common in stony meteorites.

Daubréelite, $FeCr_2S_4$.—This constituent is isometric and has a structure of the spinel type. It occurs together with troilite but is rather uncommon.

Lawrencite, $(Fe,Ni)Cl_2$.—Lawrencite is hexagonal (rhombohedral). It is deliquescent, turning in the air to ferric chloride and ferric hydroxide. It is very rare.

Quartz and tridymite.—The oxides quartz and tridymite (asmanite), SiO_2 , are present in small amounts in some iron and stony meteorites.

Magnetite (Fe_3O_4) and *chromite* ($FeCr_2O_4$).—These oxides are sometimes met in stones.

Breunnerite, $(Mg,Fe)CO_3$.—This is an isomorphic mixture of magnesite and siderite. It has been recorded in a stony meteorite only once, and consequently its presence in meteorites seems to be somewhat dubious.

Apatite.—The calcium phosphate, apatite, is not very rare in stones as an accessory constituent. It has sometimes been found to have the composition of the carbonate apatite, francolite.

Olivine, $(Mg,Fe)_2[SiO_4]$.—The members of the olivine group are the most abundant constituents of stony meteorites. The meteoritic olivines in most cases fall within the range of chrysolite, as defined by Deer and Wager (1939), and they usually contain about 10–15 per cent of the fayalite molecule.

Pyroxene group.—The isomorphic mixtures of the metasilicates of magnesium and ferrous iron occur in two forms: orthorhombic and monoclinic. The composition varies from enstatite (or clinoenstatite) to magnesium-rich hypersthene (or clinohypersthene). The orthorhombic forms are the more abundant in the meteorites but, contrary to terrestrial rocks, also members of the monoclinic series (clinoenstatite-clinohypersthene), are rather common. The calcium and aluminum pyroxenes—diopside-hedenbergite and augite—are comparatively rare as meteorite minerals. Their occurrence is mostly restricted to the rare achondrites, which are rich in calcium.

Feldspar group.—Pure anorthite, $Ca[Al_2Si_2O_8]$, is found in achondrites and stony-irons; and the isomorphic mixtures of the plagioclase series, ranging in composition from labradorite to oligoclase, are reported from chondrites. The other feldspars have not been stated to occur as meteorite minerals. The plagioclase feldspars are fairly

COMPOSITION AND STRUCTURE OF METEORITES

common in stones, though less abundant than the femic constituents. Maskelynite is the glassy equivalent of plagioclase.

PETROGRAPHIC CLASSIFICATION OF METEORITES

The meteorites are classified, according to the predominance of the metallic or the silicate phase, into three main groups, viz., (1) irons or siderites; (2) stony-irons or siderolites; (3) stones or aerolites. The further division of these groups is based on some characteristic features in the texture and composition of the meteorites, and a number of special names have been given to the subgroups. Because a detailed grouping is not necessary for the present purposes, the following classification is given, quoted from a paper of Daly (1943):

CLASSIFICATION OF METEORITES

- I. Irons or siderites
 - A. Nickel-poor ataxites
 - B. Hexahedrites
 - C. Octahedrites
 - D. Nickel-rich ataxites
- II. Stony-irons or siderolites
 - A. Olivine stony-irons or pallasites
 - B. Bronzite-asmanite stony-irons
 - C. Bronzite-olivine stony-irons or mesosiderites
 - D. Hypersthene-anorthite stony-irons
- III. Stones or aerolites
 - A. Chondrites
 - 1. Enstatite chondrites
 - 2. Bronzite chondrites
 - 3. Hypersthene chondrites
 - B. Achondrites
 - 1. Calcium-poor achondrites
 - a) Enstatite achondrites
 - b) Clinobronzite-olivine achondrites
 - c) Hypersthene-olivine achondrites
 - d) Hypersthene achondrites
 - e) Olivine achondrites
 - 2. Calcium-rich achondrites
 - a) Augite achondrites
 - b) Diopside-olivine achondrites
 - c) Clinohypersthene-anorthite achondrites
 - d) Hypersthene-clinohypersthene-anorthite achondrites

On the basis of their textural characteristics, the iron meteorites are generally divided into hexahedrites, octahedrites, and ataxites. These subgroups cannot, however, always be sharply distinguished

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from one another, because there occur transitional types which form a more or less continuous series.

The hexahedrites carry only kamacite and contain no taenite or plessite. Their nickel content is thus about 5–6 per cent. The kamacite is found in the hexahedrites as rounded or irregular grains.

Lamellar bands of kamacite are arranged in octahedrites according to the planes of an octahedron. These bands are clearly visible on polished and etched surfaces, and they are known as the Widmanstätten or Widmanstetter figures. The kamacite plates are usually surrounded by a thin layer of taenite, and the interstices are filled with plessite. The octahedrites are the most common of all irons. Their nickel content varies from 6 to 13 per cent.

The ataxites show no structural arrangements when investigated under the microscope. On the basis of their composition they are divided into two groups, consisting of the nickel-poor (with 5–6 per cent Ni) and the nickel-rich (10–20 per cent Ni) types.

The problem of the origin of the known textures of the iron meteorites cannot be regarded as completely solved so far. It is known, however, that the nickel-iron, at high temperatures, is able to carry considerable amounts of nickel in solid solution. With decreasing temperature the α -form (kamacite) will be separated from the γ -form (taenite) because of unmixing in a solid state. The kamacite lamellae of the hexahedrites are formed thus. Plessite represents a remainder in which the unmixing has not proceeded far enough to cause a total separation of the two phases.

The stony-irons form a transitional group between irons and stones. The abundance of the metallic and silicate phases varies continually from pure irons to pure stones. It is thus hardly appropriate to calculate an average composition for these mixtures, because the mean ratio of the two phases is about 1:1. In the iron-rich types the metallic phase coheres in both the space and the plane of a polished section, whereas in the more silicatic varieties it coheres only in space and not in the section. The mineralogical composition of the silicate phase is used as a basis for further subdivision of the stony-irons, as shown in the foregoing classification.

The stones are divided into two main groups according to their textural features. The first of these groups—the chondrites—is distinguished by a peculiar structure commonly found among the aerolites. Their mass is made up of rounded grains or their aggregates, called chondrules. In some meteorites the chondrules are rare, but

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in others they form almost the entire mass. The chondrites almost always contain olivine. They are further divided according to the chief pyroxene variety that is present. In the achondritic stones which form the second group no chondrules are present. The achondrites are divided into calcium-poor and calcium-rich types according to their mineralogical composition. In the second subgroup, plagioclase (anorthite) and calcium-bearing pyroxenes play an essential role in the mineralogical composition.

AVERAGE COMPOSITION OF THE VARIOUS METEORITE TYPES

The approximate knowledge of the mean chemical composition of the different meteorite types is very important in geochemical studies and calculations. As a matter of fact, rather reliable averages for the different types may be calculated on the basis of the considerable number of individual analyses now available of the different meteorites. The figures obtained from these calculations, carried out by several authors, differ from one another to some extent. Because the deviations in the values of the main constituents of the meteorites are not essentially important for the present purpose, separate averages given in literature will not be discussed in detail here. Following the presentation given by Daly (1943), the averages calculated for irons by Farrington (1911), for chondrites by Merrill (1916), and for achondrites by Washington (1925) are presented in Table 1.3. This table also contains the averages for siderites calculated by Buddhue (1946*a*) and for the silicate phase of aerolites, calculated by Brown and Patterson (1947*a*). Similarly, the latter's (1947*b*) iron, nickel, and cobalt averages are included for iron meteorites and for the metal phase of stony meteorites and are calculated by adjusting the sum of these three metals to 100 per cent. For reasons given previously, no averages calculated for the stony-irons are given in Table 1.3.

The most conspicuous feature of all meteorites, as far as their chemical composition is concerned, is the fact that they are almost completely devoid of water. In this respect they differ from all rocks of terrestrial origin. The comparison of the analyses of the metal-free chondrites and the achondrites given in Table 1.3 shows that the chondrites are considerably lower in alumina, lime, and silica than are the achondrites. This condition is responsible for the greater abundance of the calcium-aluminum pyroxenes and for the

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anorthitic composition of the plagioclase in the achondritic stony meteorites.

It should also be noted that the meteorites represent an appreciably more reducing environment than do the terrestrial rocks. This

TABLE 1.3
AVERAGE CHEMICAL COMPOSITION OF METEORITES

CONSTITUENT	IRON (FARRINGTON)	IRON (BUDDHUE)	IRON (BROWN AND PATTERSON)	METAL PHASE OF STONES (BROWN AND PATTERSON)	CHONDRITES (MERRILL)		ACHONDRITES (WASHINGTON)		SILICATE PHASE OF STONES (BROWN AND PATTERSON)
					Metal-bearing	Metal-free	Metal-bearing	Metal-free	
Per Cent									
Fe	90 67	89 70	90 78	88 58	12.15		1.18		13.25*
FeO					14 79	17 15	15.86	16.11	
Ni	8 50	9 10	8 59	10 69	1 57		0 33		0.50
NiO									
Co	0 59	0 62	0 63	0 71	0 07		0.04		0.03
CoO									
Cu		0 04							
SiO ₂					39.24	45.52	48.93	49.70	46.26
Al ₂ O ₃					2 92	3.40	6.15	6.25	3.45
Cr ₂ O ₃					0 48	0 54	0 45	0.46	0 51
MnO							0 23	0.23	0.38
MgO					22.99	26.70	18 17	18.45	27.56
CaO					2 45	2 84	7.12	7 24	2.90
Na ₂ O					0 89	1.03	0.67	0.68	1.10
K ₂ O					0.21	0.24	0.27	0 27	0.25
S	0 04	0.08			1 82	2 10	0 54	0.55	
P	0 17	0.18					0.06	0 06	0.17
P ₂ O ₅					0 27	0 31			
TiO ₂									0 15
C	0 03	0.12			0.15	0 17			
H ₂ O									0.59
Misc.		0.34							
Total	100 00	100.18	(100.00)	(99 98)	100 00	100.00	100 00	100.00	(97.10)

* From FeO and Fe₂O₃.

fact is indicated by the universal presence of unoxidized nickel-iron even in the aerolites. The iron present in the silicate structures is mostly ferrous iron, and the proportion of ferric iron is decidedly smaller than in terrestrial rocks. Another proof of the low redox potential is the presence of such minerals as schreibersite, oldhamite, lawrencite, etc., which, under the conditions prevailing in the lithosphere, would be oxidized to phosphates, sulfates, ferric oxide, etc.

COMPOSITION AND STRUCTURE OF METEORITES

The average mineralogical composition of iron meteorites, chondrites, and achondrites is presented in Table 1.4, based on the values of Table 1.3. Table 1.4 is from Daly (1943).

THE SULFIDE PHASE OF THE METEORITES

The petrographic description of the meteorites shows that the silicate meteorites, irons, and stony-irons also contain sulfides, viz., oldhamite, daubréelite, and troilite. Among these meteorite minerals, oldhamite occurs as an accessory constituent and only in the form of

TABLE 1.4
AVERAGE MINERALOGICAL COMPOSITION OF METEORITES

METEORITE MINERAL	IRONS	CHONDRITES		ACHONDRITES	
		Metal-bearing	Metal-free	Metal-bearing	Metal-free
	Per Cent				
Free metal	98.34	10.58		1.57	
Olivine		42.31	47.34	12.82	13.03
Pyroxenes		28.91	32.40	62.25	63.24
Anorthite		3.34	3.73	13.23	13.44
Albite		7.37	8.20	5.83	5.92
Orthoclase		1.11	1.24	1.69	1.72
Troilite	0.12	5.01	5.58	1.53	1.55
Schreibersite	1.12			0.40	0.41
Chromite		0.70	0.73	0.68	0.69
Cohenite	0.42				
Apatite		0.67	0.73		
Total	100.00	100.00	100.00	100.00	100.00

separate grains scattered throughout the stony mass. Troilite, however, is met in all types of meteorites as small rounded or oval-shaped aggregates and is usually accompanied by schreibersite and daubréelite. The size of these globules amounts mostly to a few millimeters or a couple of centimeters in diameter, but sometimes they can reach considerably greater dimensions. The iron sulfide found in the globules never forms separate meteorites where it would occupy the entire mass. The reason for the nonexistence of pure sulfide meteorites apparently lies in the fact that iron sulfide would be completely oxidized in the Earth's atmosphere during the flight of the meteor, because of the heating-up of the body by friction against the air. Consequently, the meteor would be completely con-

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sumed before reaching the Earth's surface. Troilite can evidently be preserved only under a metal or silicate cover. Thus, it is not known whether pure troilite meteorites exist at all. However, the fact may be emphasized that there is no evidence favoring the assumption that the sulfide and iron phases of meteoroids would be quantitatively comparable with each other.

AVERAGE COMPOSITION OF ALL METEORITES

As pointed out previously, the present views of the relative terrestrial and cosmic abundance of the elements are based, in large part, on the information concerning the mean composition of all meteorites. The composition representing the entire meteoritic matter can be calculated if the averages for the different meteorite types are known and if the relative abundance of these types can be estimated in addition. A review of the average composition of the most important meteorite groups has been given on the foregoing pages. The relative abundance of the meteorite types given in this classification will be estimated next. A problem of fundamental importance is the estimation of the abundance relationships of the iron and stony meteorites. The stony-irons, being composed of metal plus silicate, will not be treated separately in the following discussion.

The inspection of meteorite collections and catalogues reveals the fact that the known iron meteorites are far more numerous than are the stones. This result is based on the grand total of all known meteorites, regardless of whether they have been actually observed to fall or have been found and later recognized to be meteorites. However, the experience shows that the iron meteorites, owing to their unusual appearance, are likely to attract more attention from laymen and also from the scientists not too familiar with meteorites than are the ordinary-looking stones. Accordingly, it is evident that more iron meteorites than others have been reported to scientists and brought to museums. Consequently, the true abundance of irons and stones cannot be calculated from all known meteorites but only from those that have actually been observed to fall.

Besides the number of the observed meteorite falls, the mass of the individual meteorites must also be taken into account. On the basis of the falls recorded, Borgström (1937) and Watson (1941) give lists of the abundance of the various meteorite types as shown in Table 1.5.

The figures reported by Borgström and Watson show certain

COMPOSITION AND STRUCTURE OF METEORITES

inconsistencies, the source of which is apparently the degree of completeness of the available data. However, their estimates show that the stones are by far the most abundant of all meteorite types. Because the average mass of an iron meteorite is nearly twice the mass of a stone, it is not possible, according to Watson, to obtain a true value of the ratio between falling stones and irons. He estimates, however, that the stones are from four to nine times as abundant as the irons. Similarly, Goldschmidt (1937*b*) assumed the ratio of stones to irons to be 5:1. According to Nininger (1938), the ratio of aerolites to siderites is 86:14, or approximately 6:1; but some meteorite types, which have previously been regarded as very rare, may

TABLE 1.5
ABUNDANCE OF METEORITE TYPES

BORGSTRÖM		WATSON	
Type	Per Cent by Weight	Type	Per Cent by Weight
Irons	8 1	Irons...	5
Mesosiderites and pallasites	5 0	Stony-irons	1 5
Chondrites.	83 0	Stones	93 5
Magnesium-rich achondrites	0 9	Total...	100 0
Calcium-rich achondrites	3 0		
Total	100 0		

be much more abundant, possibly so much that the correct knowledge of their amount would affect the average composition of all meteorites. For the simple reason that such types are more difficult to recognize, even by trained scientists, they are considered less abundant than they really are.

A number of calculations of the average chemical composition of all meteorites is presented in literature. They have been made with due consideration of the most probable values of the abundance ratios of the metal and silicate phases in meteorites. Of such calculations, only those put forward by Goldschmidt (1937*b*) and Watson (1939, 1941) are presented here (Table 1.6). Additional abundance values for the trace elements of the meteorites will be given in Table 2.3. Goldschmidt's calculation is based on the following abundance ratio—silicate:metal:sulfide=10:2:1. The individual figures in Goldschmidt's averages were obtained from various sources and were checked by means of his own data. Watson's

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calculations are based on the mean composition of stony meteorites given by Merrill (1930) and on that of irons presented by Noddack and Noddack (1930), 5 per cent troilite being subtracted from their figures.

TABLE 1.6
AVERAGE COMPOSITION OF ALL METEORITES

ELEMENT	RATIO OF STONES TO IRONS		
	4 1 Watson (1939)	5 1 Goldschmidt (1937b)	9 1 Watson (1941)
	Per Cent		
O	29 00	32 30	32.70
Si.	14 40	16 30	16 28
Fe	38.00	28 80	31 85
Mg	11 00	12 30	12 88
S	1 90	2 12	1 87
Al	0 61	1 38	0.68
Ca	1 10	1 33	1 18
Ni	2 80	1 57	2 08
Na	0.24	0.60	0.27
Cr	0.12	0 34	0 12
K.	0 06	0 15	0 06
Mn.	0 15	0 21	0.16
Cl	0 02	0 10-0 15?	0 03
P.	0 11	0.11	0 10
Ti	0 08	0 13	0 09
Co	0 22	0.12	0.18
C.	0 14	0.03	0 15

The averages presented in Table 1.6 give a general view of the mean composition of meteorites. The differences among the three analyses also indicate the degree of accuracy obtained in the calculation. The principal uncertainty affecting all estimates of the average composition of the meteorites is due to difficulties in the determination of the relative amounts of the meteorite phases.

APPENDIX: TEKTITES

Certain glassy bodies are found in various parts of the world in Quaternary and Tertiary deposits. These bodies, apparently irrelevant to the sediments in which they lie imbedded, are rounded, oblong, or more irregularly shaped, and their forms seem to imply an origin through solidification from a viscous melt. These bodies, which are called tektites, measure usually only a few centimeters in diameter. Their origin is still problematic, and different hypotheses

COMPOSITION AND STRUCTURE OF METEORITES

have been presented to account for them. However, the extramundane origin of the tektites seems to be very possible, although no conclusive evidence has, so far, been adduced.

Petrographically, the tektites consist almost exclusively of glass, containing only minute amounts of crystallites. Chemically, they

TABLE 1.7

AVERAGE COMPOSITION OF TEKTITES	
Constituent	Per Cent
SiO ₂	77.29
Al ₂ O ₃	11.07
(Fe,Mn)O....	3.21
MgO.....	0.99
CaO.....	2.21
Na ₂ O.....	0.45
K ₂ O.....	2.48
Total	97.70

differ pronouncedly from the meteorites proper and from terrestrial igneous rocks as well. They resemble, in some respects, the aluminum-rich argillaceous sediments. An average of twelve individual tektite analyses, calculated by Linck (1924), is presented in Table 1.7. On the average, the content of silica and alumina is higher in tektites than in terrestrial igneous rocks and argillaceous sediments. The presence of an excess of alumina, as compared with lime and the alkalies, is evident.

ABUNDANCE OF ELEMENTS AND NUCLIDES

ABUNDANCE CALCULATIONS

THE Sial crust, which is the surface layer of the silicate shell of the Earth (the lithosphere), is composed of three groups of rocks of different origin: igneous rocks, sediments and sedimentary rocks, and metamorphic rocks. The last-mentioned rocks are either of magmatic or of sedimentogenic origin and are, like the sediments, formed of material ultimately produced by igneous rocks. Consequently, the average chemical composition of the Sial crust is very nearly equal to the average composition of igneous rocks. It is true that, by the processes of weathering and the formation of sediments, some oxygen, water, and carbon dioxide are removed from the atmosphere and hydrosphere and correspondingly modify the composition of the upper lithosphere; but experience has shown that the amounts in question are, quantitatively, rather unimportant and may accordingly be neglected when the average chemical composition of the upper lithosphere is calculated.

The first attempt to calculate the chemical composition of the Earth's crust on the basis of the composition of the igneous rocks was made by Clarke (1889). He calculated the mean composition of 880 igneous rocks from various countries. Later, Clarke and Hillebrand (1897) calculated a new average, using analyses of 680 American igneous rocks, and Harker (1899) based an average on 397 British igneous rocks, followed (1904) by another average calculated from the analyses of 536 igneous rocks of Great Britain. All these averages, however, were unreliable because many old and doubtful analyses were used in their calculation and the number of the analyses averaged was rather low. New averages were accordingly calculated and published by many geologists. Washington (1903) averaged 1,811 rock analyses from all parts of the world, and Clarke offered new re-

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vised averages in the successive editions of his book *The Data of Geochemistry*. Daly (1910, 1914) also presented a new value for the average composition of igneous rocks.

The most prominent among the new calculations is the average presented by Clarke and Washington (1922, 1924), which was based on 5,159 analyses of igneous rocks from all parts of the world. They also gave areal averages for the composition of the Earth's crust in

TABLE 2.1
CHEMICAL COMPOSITION OF THE LITHOSPHERE
ANALYSIS OF OPDALITE

CONSTITUENT	IGNEOUS ROCKS (CLARKE AND WASH- INGTON)	CORDIL- LERAN AND APPALACH- IAN ROCKS (KNOPF)	PRE-CAM- BRIAN ROCKS OF FINLAND (SEDER- HOLM)	IGNEOUS ROCKS (VOGT)	CANADIAN SHIELD (GROUT)	GLACIAL AND POST- GLACIAL CLAYS OF NORWAY (GOLD- SCHMIDT)	OPDALITE, SOUTHERN NORWAY (GOLD- SCHMIDT)
	Per Cent						
SiO ₂	59.14	61.64	67.45	64.9	63.08	59.19	61.95
Al ₂ O ₃	15.34	15.71	14.63	15.55	16.75	15.82	15.30
Fe ₂ O ₃	3.08	2.91	1.27	2.15	2.38	} 6.99	0.94
FeO.....	3.80	3.25	3.13	2.5	2.91		4.57
MgO.....	3.49	2.97	1.69	2.45	1.78	3.30	4.10
CaO.....	5.08	5.06	3.39	4.3	4.07	3.07	4.66
Na ₂ O.....	3.84	3.40	3.06	3.45	3.64	2.05	3.43
K ₂ O.....	3.13	2.65	3.55	3.65	3.07	3.93	3.37
H ₂ O.....	96.90	97.59	98.17	98.95	97.68	94.35	98.32
TiO ₂	1.15	1.26	0.79		0.79	3.02	0.55
P ₂ O ₅	1.05	0.73	0.41	0.55	0.81	0.79	0.96
MnO.....	0.30	0.26	0.11	0.175	0.22	0.22	0.16
	0.12	0.16	0.04		0.02		0.07
Total.....	99.52	100.00	99.52	99.675	99.52	98.38	100.06

different countries and continents. Their calculation, even today, is used as a basis of various geochemical considerations. It is presented in Table 2.1.

As far as information was available, Clarke and Washington also collected and published evidence concerning the abundance of many other elements not included in the average. Their results laid the basis of the fact already known qualitatively, viz., that eight elements constitute the bulk of the upper lithosphere. These main elements are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. When calculated as elements, the values

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of Clarke and Washington presented in Table 2.1 yield the composition for the igneous rocks shown in Table 2.2, which also shows the composition, in per cent by volume, as recalculated by Barth (1948) on a water-free basis.

All other elements, called, as a group, accessory or minor or trace elements, form only 1.72 per cent of the total mass of the igneous rocks. The most abundant among them, viz., titanium, phosphorus, hydrogen, and manganese, comprise 1.13 per cent, and consequently no more than 0.59 per cent is left for by far the greatest part of the elements.

TABLE 2.2
THE EIGHT MAIN CONSTITUENTS
OF IGNEOUS ROCKS

Element	Per Cent by Weight	Per Cent by Volume
O.....	46.42	91.83
Si.....	27.59	0.83
Al.....	8.08	0.79
Fe.....	5.08	0.58
Ca.....	3.61	1.50
Na.....	2.83	1.64
K.....	2.58	2.19
Mg.....	2.09	0.58
Total.....	98.28	99.94

All the calculations outlined above were based on the assumption that the arithmetic mean of all analyses would give a reliable picture of the chemical composition of the outermost crust of the Earth, often called the ten-mile crust. However, even the earliest averages met with well-grounded criticism. Harker (1899) was the first to emphasize the fact that the principles of selection of the analyzed samples may disturb the values and that no selection should be exercised. Mennell (1904) pointed out that the relative abundance of the different rock classes must be duly considered. He also stressed the preponderance of granite in the Earth's crust and claimed that in the calculations of Clarke and Harker basic rocks had received excessive weight. In a later paper Mennell (1909) laid further stress on his viewpoint and emphasized the fact that exceptional types are largely represented by analytical data among rocks of all classes. Daly (1910) also emphasized the abundance of granites in the Earth's crust.

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Loewinson-Lessing (1911) found all previous results arbitrary because the method was wrong in principle and because the relative quantities of the igneous rocks had not been considered in the average calculations. He also suggested that the Earth's crust was derived from two fundamental magmas, a granitic and a basaltic one, present in approximately equal amounts, and that the average composition of the igneous rocks and probably that of the entire outer part of the crust corresponded nearly to a syenitic magma. Mead (1914) concluded that igneous rocks collected for petrographic purposes would include too many unusual and interesting rock types to give a true average, and he suggested that a mixture of 65 per cent average granite and 35 per cent average basalt had a composition very close to the general average of all igneous rocks as computed by Clarke.

In the meantime, Clarke (1916) had already noted the criticism and had stated that the whole land surface of the Earth must be considered in order to get a true average. The first attempt to calculate an average based on the quantitative distribution of rocks was made by Knopf (1916). He calculated the average chemical composition of Appalachian and Cordilleran rocks, based on Daly's averages, by dividing the area occupied by the various types by the total area of igneous rocks. This gave a weight factor, which was used to multiply the average composition of the rock species, and thus the percentage contribution of the species to the composition of the average igneous rock was obtained. The average thus calculated by Knopf is presented in Table 2.1.

Still stronger criticism with reference to the method of simply averaging analyses of igneous rocks was offered by Sederholm (1925), who also emphasized that in such calculations the differences in the distribution of the rocks passed unnoticed. Sederholm pointed out that it is natural, because of human curiosity, for the petrographers to pay considerably more attention to rocks of extraordinary mineralogical and chemical composition and of restricted occurrence, e.g., alkalic and hypabyssal rocks. Consequently, such rocks, in calculations carried out according to the method of simple averaging used by Clarke and Washington, affect the result more than their actual distribution would demand.

In order to establish the special chemical characteristics of the Basement Complex of Finland, as compared with the upper lithosphere as a whole, Sederholm carried out the calculation of the aver-

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age chemical composition of the Earth's crust of Finland at that time. He used the general geological map of Finland to determine the distribution of the most important types of rocks and calculated their average composition on the basis of chemical analyses available. In his averages were also included the figures for metamorphic rocks, e.g., schists, quartzites, and limestones. The result obtained by Sederholm is presented in Table 2.1.

Referring to the viewpoints repeatedly discussed above, Vogt (1931) presented a new calculation of the average composition of plutonic rocks, which is given in Table 2.1. This average was calculated partly on the basis of the mean chemical composition of the various types of igneous rocks presented by Daly (1914) and partly on the basis of Vogt's own computations. In his average Vogt used amounts of plutonic rocks which were proportional to the relative distribution of their masses.

Still another average was calculated by Goldschmidt (1933*a*), based on the composition of samples furnished by Nature herself, viz., 78 Glacial and post-Glacial clays from Norway, formed mainly by mechanical disintegration. The use of such material was considered by Goldschmidt to be legitimate because by far the greatest part of the argillaceous material had been formed by the disintegration of igneous and metamorphic rocks and thus represented, as such, the average composition of the geological units in question and because chemical weathering had played only a subordinate role in their formation. Goldschmidt's average is given in Table 2.1.

Grout (1938) published a preliminary estimate of the composition of the Earth's crust in the Canadian Shield. In his average, as in that of Sederholm, sedimentary and metamorphic rocks of the area were also included. The result indicates a granodioritic composition, but it is possible that too much attention has been paid to rocks of granitic composition.

If the values presented in Table 2.1 are compared with one another, a well-pronounced difference is found to exist between Sederholm's average and that calculated by Clarke and Washington. The Earth's crust in Finland is considerably more silicic than the Sial crust, on an average, and corresponds most nearly to the average composition of granodiorite. This is due mainly to the fact that granite is the prevalent plutonic rock and that extensive areas of plateau basalts and of basaltic rocks in general are absent in the pre-Cambrian formations of Finland. These rocks, on the other hand, are

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rather common in geologically younger formations and constitute a notable part of all igneous rocks, being the most abundant among basic rocks. According to Sederholm, it is probable that the scarcity of basaltic rocks is a phenomenon proper to all pre-Cambrian terranes because of their deeper-reaching denudation. Acidic igneous rocks of granitic and granodioritic composition predominate, as a rule, in the root zones of mountain chains. Their melts are produced from the parental magma by directed pressure and movements, but they may also result in granitization.

The averages calculated by Knopf, Vogt, and Grout are also more silicic than that given by Clarke and Washington, although the difference is less pronounced than in the previous case. If the average calculated by Goldschmidt is compared with that given by Clarke and Washington, only the content of calcium and sodium is found to be materially different. This is due to the extraction of these metals during the weathering processes, one of the most important geochemical phenomena connected with their cycles. The other differences are rather unimportant, and hence Goldschmidt's average corresponds closely to the mean chemical composition of the upper lithosphere.

An igneous rock which corresponds in its chemical composition to the average calculated for the upper lithosphere is opdalite from the Opdal-Indset in southern Norway. Goldschmidt (1933*a*) gives two chemical analyses of this rock, and their partial average is included in Table 2.1.

Among the averages presented in this table, the values of Clarke and Washington, Knopf, and Goldschmidt are rather coherent, whereas those given by Vogt and Grout and especially the value calculated by Sederholm give a notably different picture of the composition of the Sial crust. It is not easy to decide which of these values is to be preferred, and so far no general agreement about this point has been reached. However, it is possible that the average of Clarke and Washington represents a somewhat too basic composition and that the average composition of the uppermost part of the lithosphere should consequently be more silicic. So far, this question cannot be finally settled, and hence their result, which is commonly used, will be applied also in this book when the whole Sial crust, or the average igneous rock, is dealt with. On the other hand, Sederholm's value will be used when the composition of the Basement Complex both in pre-Cambrian and in younger orogenic zones is considered.

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In all averages presented in Table 2.1, chiefly the eight principal elements of the Earth's crust have been considered. This is due to the fact that these averages have been calculated solely on the basis of chemical rock analyses. Estimates of the amount of many trace elements were furnished earlier by Clarke (1889) and Vogt (1898, 1899) and later by Clarke and Washington (1922, 1924); but most, if not all, of the numbers given by these scientists must now be considered obsolete. Consequently, for many elements, they do not give too reliable a picture of the abundance.

But, with the development of new physical and chemical methods for the determination of the elements, particularly optical and X-ray spectrochemical analysis and colorimetric and radioactivity methods, the distribution and the abundance of the trace elements became known in greater detail. The most important work in this respect was carried out by Goldschmidt, Hevesy, and Paneth and their numerous co-workers and by Noddack and Noddack. Their work pertained to the determination of the abundance of the elements in the Earth's crust and in the meteorites. The work of many astrophysicists has revealed much information concerning the abundance of the elements in the solar and stellar atmospheres. The methods of analysis of the quantitative chemical composition of stellar atmospheres, first developed by American astrophysicists, are very much similar to those of spectrochemical analysis used for terrestrial material. All recent studies have, more or less, paid attention to the Periodic System as a whole, even the elements regularly met in low concentrations being included.

The most recent review of the abundance of the elements was given by Goldschmidt (1937*b*). The abundance numbers are given in Table 2.3, which is largely based on Goldschmidt's values, completed with some more recent determinations.¹

With the exception of columbium and tantalum, the abundance values in meteorites are quoted from Goldschmidt (1937*b*), who in his calculation of the average composition of the meteorites used the abundance ratio silicate:metal:sulfide = 10:2:1 (see chap. 1). In addition, the presence of some elements in meteorites is noted according to Buddhue (1946*b*). The abundance values in the solar atmosphere are calculated from the values given by Russell, Dugan,

1. Ti (Ahrens, 1947*b*); P (Conway, 1945); He (Goodman and Evans, 1944); Cb, Ta (Ran-kama, 1944, 1948*c*); N, Ne, A (Lord Rayleigh, 1939); Co, Ni, Cu, Mo, Cd (Sandell and Goldich, 1943); W (Sandell, 1946); Hg (Saukov, 1946); Cl, Br (Selivanov, 1940); F (Wasser-stein, 1947); Sr (Wickman, 1948); Zn (calculated from Lundegårdh, 1947).

TABLE 2.3

ABUNDANCE OF THE ELEMENTS IN IGNEOUS ROCKS,
IN METEORITES, AND IN THE SUN'S ATMOSPHERE

ATOMIC No. Z	ELE- MENT	IGNEOUS ROCKS		METEORITES		SUN'S ATMOSPHERE	
		g/ton	Atoms per 100 Si	g/ton	Atoms per 100 Si	100 mg·m ⁻²	Atoms per 100 Si
0	n						
1	H	Present		Present		31,600.	88,500
2	He	0 003	0 0000076	Present		4,000.	2,800
3	Li	65	0 091	4	0 010	0 0006:*	0 00024:
4	Be	6	0 0067	1	0 0020	0 0006	0 00019
5	B	3†	0.0028	1 5	0 0024	Probably present?†	
6	C	320†	0 27	300	0 33	400	93 9
7	N	46 3	0 083	Present		1,900.:	260:
8	O	466,000	296	323,000	347	15,900	2,732 5
9	F	600-900	0 32-0 48	28	0 021	Probably present?	
10	Ne	0 00007	0 000000035	Present?		Absent	
11	Na	28,300	12 4	5,950	4 42	400	48 7
12	Mg	20,900	8.76	123,000	87 24	500.	57 6
13	Al	81,300	30 5	13,800	8 79	60.	6 2
14	Si	277,200	100	163,000	100	1,000.	100
15	P	1,180	0 38	1,050	0 58	0 3:	0.027.
16	S	520	0 16	21,200	11 4	16:	1 4:
17	Cl	314	0 09	1,000-1,500:	0 4-0 6:	Absent	
18	A	0 04	0 00001	Present?		Absent	
19	K	25,900	4 42	1,540	0 69	250.:	17 9.
20	Ca	36,300	9 17	13,300	5 71	200	14 0
21	Sc	5	0 0011	4	0 0015	0 2	0 0124
22	Ti	4,400	0 92	1,320	0 47	8.	0 47
23	V	150	0 030	39	0 013	5	0 27
24	Cr	200	0 039	3,430	1 13	25	1 35
25	Mn	1,000	0 18	2,080	0 66	40	2 05
26	Fe	50,000	9.13	283,000	89 1	1,000.	50 13
27	Co	23	0 004	1,200	0 35	25	1 19
28	Ni	80	0 014	15,680	4 60	60.	2 86
29	Cu	70	0.011	170	0 046	6	0 26
30	Zn	132	0 020	138	0 036	5	0 21
31	Ga	15	0 0022	4 2	0 00034	0 006:	0 00024:
32	Ge	7	0 00095	79	0 0188	0 08	0 0031
33	As	5	0 00067	Present		Absent	
34	Se	0 09	0 000012	7	0 0015	Absent	
35	Br	1.62	0 00020	20	0 0043	Absent	
36	Kr					Absent	
37	Rb	310	0.036	3 5	0 00068	0 004:	0 00013:
38	Sr	300	0.035	20	0 0040	0.16	0 005
39	Y	28 1	0 00307	4 72	0.000974	0 03	0 0009
40	Zr	220	0 026	73	0 0139	0 03	0 0009
41	Cb	24	0 0026	0 41	0.000076	0 001:	0.00003:
42	Mo	2 5-15	0 0003-0 0016	5.3	0 00095	0 0025	0 00007
43	Tc	Presence unsettled				Presence unsettled	
44	Ru	Present		2 23	0 00036	0 005	0 00014
45	Rh	0 001	0 00000010	0 80	0 00013	0 0003	0 000003
46	Pd	0 010	0 0000009	1 54	0 00025	0 0013	0 00003
47	Ag	0 10	0 000009	2 0	0 00032	0 001	0 000028
48	Cd	0 15	0 000013	Present		0 016	0 0004
49	In	0.1	0 000007	0 15	0.000023	0 0001:	0 0000028:
50	Sn	40	0 00343	20	0 00291	Probably present	
51	Sb	1:	0 000083:	Present		0 0008:	0 000018:
52	Te	0 0018:		0 1:		Absent	
53	I	0 3	0 000024	1	0 000136	Absent	
54	Xe					Absent	
55	Cs	7	0 00053	0 08	0 000010	Absent	
56	Ba	250	0 018	6 9	0 00083	0 25	0 005
57	La	18 3	0.00128	1 58	0 000208	0 008	0 00017
58	Ce	46 1	0 00321	1 77:	0 000232:	0 04	0 0008
59	Pr	5 53	0 000389	0 75	0 0000964	0 0006.	0 000012:
60	Nd	23 9	0 00162	2 59	0 000331	0 016	0 0003
61	Pm	Presence unsettled				Presence unsettled	
62	Sm	6 47	0 000419	0 95	0 000115	0 005	0.000093
63	Eu	1 06	0 000068	0 25	0 000028	0.004:	0 000074:
64	Gd	6 36	0 000394	1.42	0 000165	0 002:	0 000036:
65	Tb	0.91	0 000056	0 45	0 000052	Probably present	
66	Dy	4 47	0 000269	1 80	0 000203	0 006:	0.0001:

*: = Uncertain value.

† Considerably higher content in sedimentary rocks.

‡ ? = More doubtful value.

TABLE 2.3—Continued

Atomic No. Z	ELE- MENT	IGNEOUS ROCKS		METEORITES		SUN'S ATMOSPHERE	
		g/ton	Atoms per 100 Si	g/ton	Atoms per 100 Si	100 mg·m ⁻²	Atoms per 100 Si
67	Ho	1 15	0 000068	0 51	0 000057	Presence	unsettled
68	Er	2 47	0 000144	1 48	0 000163	0 0002	0 000003
69	Tm	0 30	0 0000115	0 26	0 000029	0 0005.	0 000008
70	Yb	2 66	0 000149	1 42	0 000150	0 0016.	0 000026
71	Lu	0 75	0 000037	0 46	0 000048	0 0016	0 000026
72	Hf	4 5	0 00030	1 6	0 00015	0 0004	0 000006
73	Ta	2 1	0 00012	0 30	0 000028	Probably present	
74	W	1 5-69	0 000032-0 0038	15	0 00145	0 0003	0 0000046
75	Re	0 001	0 000000054	0 0020	0 00000018	Absent	
76	Os	Present		1 92	0 000174	0 0006	0 0000088
77	Ir	0 001	0 000000005	0 65	0 000058	0 0001?	0 0000014?
78	Pt	0 005	0 00000027	3 25	0 000287	0 007	0 00010
79	Au	0 005	0 00000026	0 65	0 000057	Probably present	
80	Hg	0 077-0 5	0 0000039-0 000025	Present		Absent	
81	Tl	0 3-3	0 000015-0 00015	Present		Absent	
82	Pb	16	0 00080	11	0 00091	0 003	0 00004
83	Bi	0 2	0 000009	Present		Absent	
84	Po	0 0000000003	14·10 ⁻¹⁵	0 00000000003	2·10 ⁻¹⁵	Absent	
85	At	Present				Presence unsettled	
86	Rn	Present		Present		Absent	
87	Fa	Present				Presence unsettled	
88	Ra	0 0000013	58·10 ⁻¹²	0 0000001	76·10 ⁻¹³	Absent	
89	Ac	0 0000000003	13·10 ⁻¹⁵	0 00000000002	15·10 ⁻¹⁶	Absent	
90	Th	11 5	0 00050	0 8	0 000059	Present	
91	Pa	0 0000008	35·10 ⁻¹²	0 00000006	45·10 ⁻¹³	Absent	
92	U	4	0 00016	0 36	0 000023	Presence unsettled	
93	Np	Probably present				Presence unsettled	
94	Pu	Present				Presence unsettled	
95	Am	Probably present				Presence unsettled	
96	Cm	Probably present				Presence unsettled	

and Stewart (1938), completed with the information presented by Russell and Moore-Sitterly (1943). Strömgren (1940) has calculated the abundance of H, Mg, Ca, Na, and K in the solar atmosphere. If his values are recalculated on the basis of atoms per 100 atoms of silicon, and if the H:He abundance ratio is supposed to be 5:1, the values given in Table 2.4 are obtained. This table also contains, for the sake of comparison, the values for the abundance of the light elements in the atmosphere of the star τ Scorpii given by Unsöld (1941). With reference to the elements announced to be absent in the Sun, only Re, Tl, and Bi are really absent, whereas in the case of Cs, As, Hg, Te, Se, I, Br, Xe, Cl, Kr, A, and Ne the high excitation potential of the accessible spectrum line is the cause of conditions unfavorable for their appearance in the solar spectrum; and in the case of the radioactive elements Po, Rn, Ra, Ac, and Pa the abundance is too low (Russell and Moore-Sitterly, 1943).

The values for some elements, e.g., Te, Sb, and W, are still unreliable. Most of the abundance determinations are based on composite mixtures of igneous rocks. However, many elements which are not known to be present in volcanic emanations have been determined in composite mixtures made of argillaceous sediments, because the

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amounts present therein are certainly derived from disintegrated igneous and metamorphic rocks. This is the case with the following elements: Be, Sc, Ga, Ge, Y, La, the rare-earth metals, Hg (upper limit), and Th.

The investigation of the abundance relationships of the elements on the basis of the values given in Table 2.3 reveals a picture which differs in many respects from the conventional opinion in this matter. In everyday practice the commonness or the rarity of a given element is usually mistaken for the degree of its use in research laboratories

TABLE 2.4
ABUNDANCE OF THE LIGHT ATOMS IN THE ATMOSPHERES
OF SUN AND τ SCORPII

Z	ELEMENT	SUN'S ATMOSPHERE (ATOMS PER 100 Si)	ATMOSPHERE OF τ SCORPII	
			Relative Masses $\times 10^{-20}$	Atoms per 100 Si
1..	H	4,800,000	219,000	1,564,000
2 .	He	960,000	155,000	277,900
6 .	C		457	271 4
7.....	N		1,180	592 9
8.....	O		3,400	1,582 6
10	Ne		4,900	1,750 0
11 ..	Na	4 2		
12 .. .	Mg	180	310	92 9
13... .	Al		21 4	5 71
14 .	Si		390	100
19 .	K	0 96		
20 .	Ca	7 8		
26 .. .	(Fe)		(560)	(71 4)

and technical products. However, it must be emphasized that the true terrestrial and cosmic abundance of an element in only a very few cases bears any relation to its commonness in everyday life. The use and the technical value of an element is affected both by its physical and chemical properties, which cause its usefulness for man, and by the possibilities of obtaining the element in noteworthy quantities and in the proper degree of purity from its ores. It is readily understood that these demands depend decisively on the manner of occurrence of the element and on the ease with which it can be separated from other elements accompanying it in Nature. An illustrative example of the discrepancy between the true and the apparent abundance is displayed by the metals cadmium and europium. Their abundance numbers, given in Table 2.3, show that europium, one of

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the rare-earth metals, is approximately seven times as abundant as the technically important cadmium. Cadmium was discovered in 1817 and europium as late as 1901. This fact and the more extensive knowledge of the chemical properties of cadmium is due to its common occurrence in sphalerites, in which it is strongly enriched; hence

TABLE 2.5
ORDER OF THE ATOMIC ABUNDANCE OF THE
MOST ABUNDANT ELEMENTS

Abundance	Igneous Rocks (Upper Lithosphere)	Meteorites	Sun's Atmosphere	τ Scorpii	Nebula NGC 7027
Highest....	O	O	H	H	H
	Si	Si	He	He	He
	Al	Fe	O	Ne	C
	Na	Mg	N	O	O
	Ca	S	C	N	Si
	Fe	Al	Si	C	N
	Mg	Ca	Mg	Si	B
	K	Ni	Na	Mg	Ne
	Ti	Na	Fe	(Fe)	S
	C	Cr	K	Al	P
	P	K	Ca		V
	Mn	Mn	Al		Li
	S	P	Ni		Be
	F	Cl	F		Al
	Cl	Ti	Mn		Mg
	Li	Co	Cr		Cl
	Cr	C	S		Fe
	Rb	Cu	Co		Na
	V	Zn	Ti		A
	Zr	F	V		Ca
	Ba	Ge	Cu		Cr
	Sr	Zr	B		Mn
	Ni	V	Zn		Ti
	Zn	Li	P		K
			Sc		Sc
			Sr		F
Lowest.....			Ba		

this metal is readily obtained from many sphalerite ores. Europium, on the contrary, is not noticeably concentrated in any mineral deposits of technical importance. In addition, until recently its compounds could not be separated except by a long and tedious process of fractionating crystallization. Another example of the above considerations is furnished by hafnium, which is more abundant than either antimony or bismuth.

The order of the atomic abundance of some of the most frequent elements in igneous rocks, meteorites, and the Sun's atmosphere is

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given in Table 2.5. The order in the Sun's atmosphere is based on the abundance data given by Russell, Dugan, and Stewart (1938); that in the star τ Scorpii is from Unsöld (1941); and that in the nebula NGC 7027 is from Bowen and Wyse (1939). It should be noticed, however, that, in the last two instances, only the abundances listed in Table 2.5 were actually determined. The values presented in this table show that in igneous rocks—that is, in the uppermost parts of the lithosphere—the eight chief elements, as a matter of fact, occupy the first places, whereas in the meteorites the group of the ten most abundant elements also includes sulfur, nickel, and chromium. If the order of abundance in the upper lithosphere is compared with that in the meteorites, other notable differences will be observed, in addition. This is readily understood because the meteorites display the true cosmic abundance of many elements in a much more satisfactory way than do the igneous rocks. According to the prevalent view, the outermost crust of the Earth was formed by a process of differentiation and, consequently, cannot represent the average chemical composition of the Universe, not even that of the Earth in its entirety.

The Earth, compared with the Sun, is notably poor in the atmosphere elements. This fact strongly suggests that vast amounts of gases escaped from the primordial atmosphere of the Earth. The order of the atomic abundance of the elements given in Table 2.5 shows that the general chemical composition of the Sun and the Earth is similar, however, with the exception of hydrogen and helium, which are enormously more abundant on the Sun. Russell (1929) was the first to emphasize the high cosmic abundance of hydrogen. According to Biermann (1943), the most probable composition of the Sun is as follows:

	Per Cent
Hydrogen.....	55
Helium.....	11
Metals.....	0.25
Carbon, nitrogen, oxygen, fluorine, neon.....	~34

The light elements, up to nitrogen or oxygen, in general are considerably more abundant in the Sun than in the Earth, but the relative proportions of the metals are much alike. As stated by Russell (1935*a*), it is hard to find a single case showing that a given metal is more or less abundant in the Sun than on the Earth. As a matter of fact, the seven principal constituents of the upper lithosphere, with the exception of oxygen, form the bulk of the heavier elements in the Sun's atmosphere as well. The relative proportions are not the same,

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but the agreement would be better if comparison could be made with the deeper layers of the Earth's crust. The abundance relationships seem to imply the possibility that the Earth is formed of solar material and that the light gases contained therein escaped before the rapid condensation of the Earth.

With reference to the meteorites, Russell (1941) finds no difference in composition between them and the Sun's atmosphere, as far as the metals are concerned. Most of the stars are very similar to the Sun in chemical composition, although in some stars there occurs a definite excess of certain elements, e.g., carbon, silicon, sulfur, strontium, and zirconium. Molecules appear in the atmospheres of the cooler stars; they include, among others, C_2 , CH, CN, and CO. Evidently, the most abundant molecule is H_2 , but its presence cannot be directly observed. It was first shown by Payne-Gaposchkin (Payne, 1925) that stars belonging to the various spectral types display marked similarities in chemical composition and that, with reference to the heavier elements, their composition closely resembles that of the Earth's crust. Unsöld (1941) found the following percentage ratios of atomic abundance in the star τ Scorpii: hydrogen:helium:all other elements = 85:15:0.24; this ratio is supposed to be valid for all main-sequence stars (Unsöld, 1948b).

Although the chemical composition of the stars may be somewhat variable, some of the abundance differences may be caused by peculiar excitation mechanisms which affect the intensity of the lines in stellar spectra. The inevitable conclusion from the cosmic evidence is that all information available strongly suggests the stability of the abundance relationships in all parts of the Universe.

The atomic abundance of some of the lighter elements, calculated per 100 atoms of silicon, in the upper lithosphere, in the meteorites, in the Sun's atmosphere, in the atmosphere of the star τ Scorpii, and in the gaseous nebula NGC 7027 are presented in Figure 2.1, which is drawn on the basis of values calculated from Tables 2.3 and 2.4 and the values given by Bowen and Wyse (1939). Figure 2.1 illustrates the fact that, in general, the courses of the abundance curves are comparable, with the exception of the curves representing the upper lithosphere and the meteorites. The deviations are readily explained by means of the recent information concerning the origin of the Earth and the meteorites. Another graph, which shows the atomic abundance of all elements in the Universe, constructed by Goldschmidt (1937b) on the basis of the values calculated for igneous

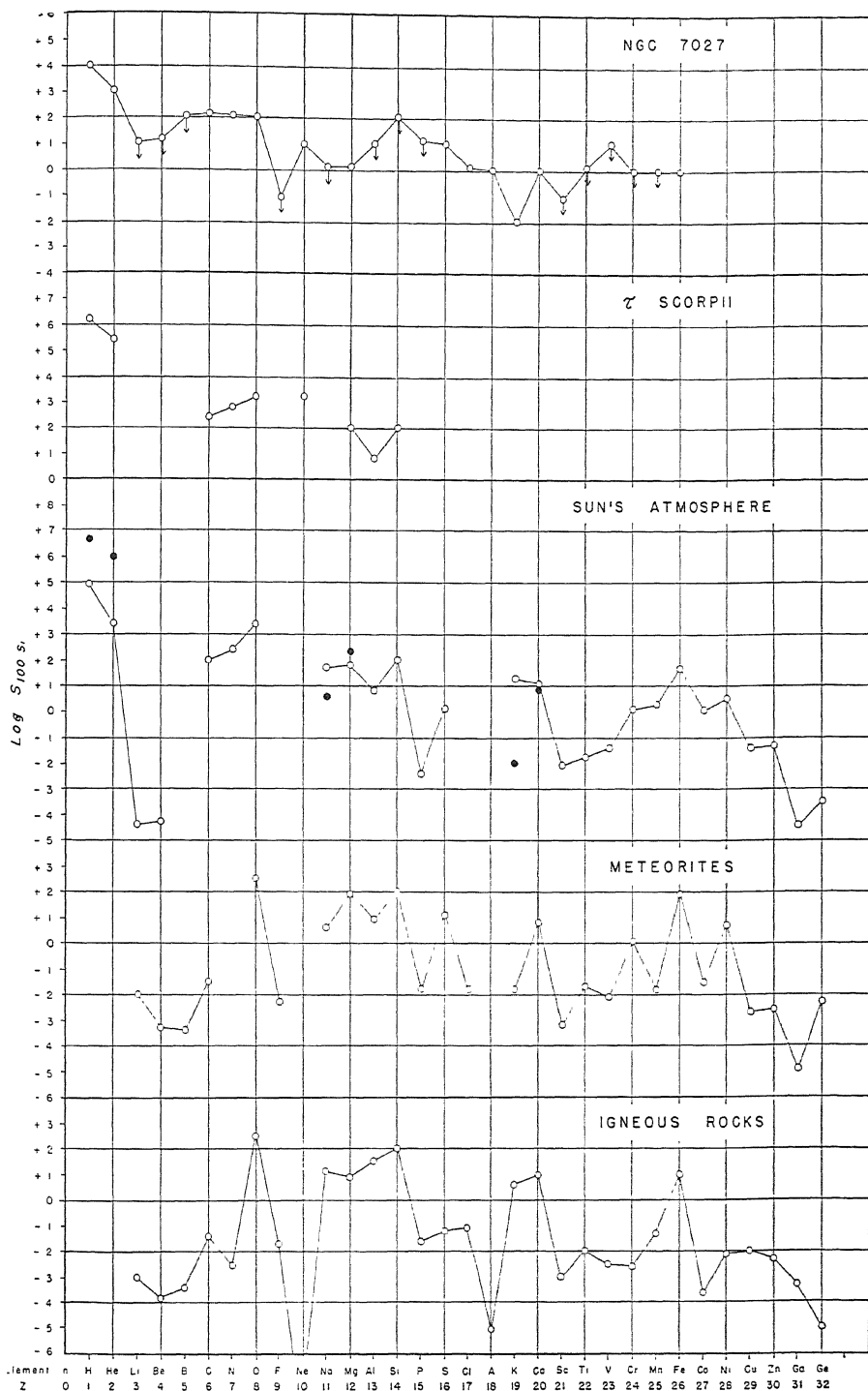


FIG. 2.1.—Cosmic abundance of the lighter elements

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rocks, the meteorites, and the Sun's atmosphere, is presented in Figure 2.2. In this figure also the abundance is calculated per 100 atoms of silicon.

The graph reproduced in Figure 2.2 shows clearly that the cosmic abundance of the elements tends to decrease with increasing atomic number. Hydrogen, the lightest atom, is also the most abundant one.

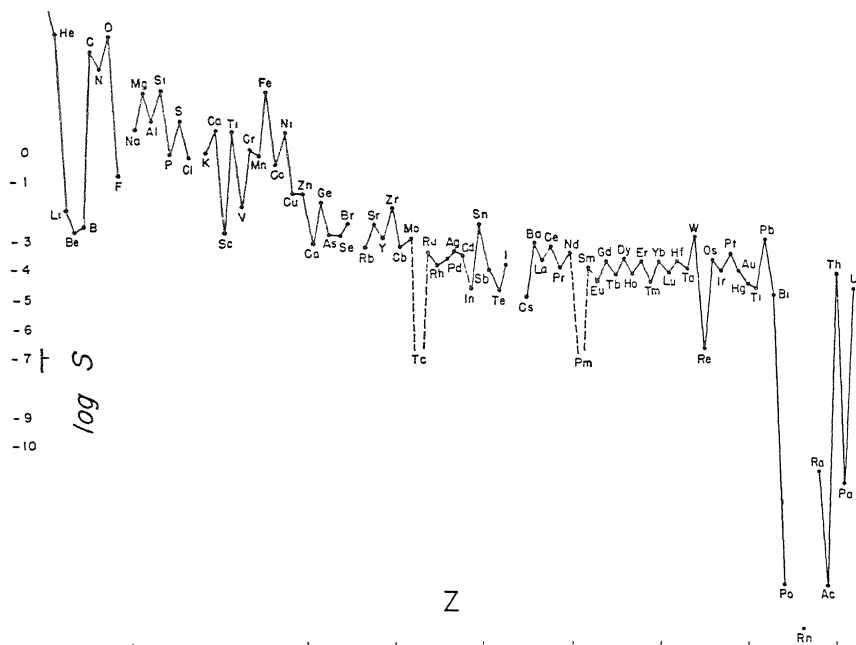


FIG. 2.2.—Cosmic abundance of the elements as a function of the proton number. *Abscissa*, proton number (Z). *Ordinate*, logarithm of the abundance ($\log S$).

However, some of the heavy atoms, viz., lead, thorium, and uranium, actually compare in abundance with many of the lighter elements. The reason is that lead is the stable decay product of the three natural radioactive series of elements and therefore accumulates. The half-life of the uranium isotopes U^{235} and U^{238} and of the thorium isotope Th^{232} is very long, and therefore these two metals decrease in quantity rather slowly.

As already stated by Harkins (1917), the abundant elements are those of low atomic weight, with an atomic number less than 29. Thus the abundance of the elements is related to their atomic number

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and not to their position in the Periodic Chart. The decrease in abundance, however, is not constant because the curve passes through a number of pronounced maxima and minima. Maxima are met, e.g., at iron, tin, and lead, and minima occur at fluorine, scandium, rhenium, etc. Two very deep minima are present, one at lithium, beryllium, and boron and the other at the rare radioactive elements. The first minimum is of high importance because it occurs in the beginning of the Periodic System, where the abundance of the elements usually is rather high.

The curve in Figure 2.2 also shows the regularity known as the rule of Oddo and Harkins, which, with few exceptions, controls the abundance of the elements. It is based on the observation of Oddo (1914) that elements whose atomic weights, rounded off to their closest integers, are divisible by 4 form the bulk (approximately 86.5 per cent) of the mass of the upper lithosphere. In like manner the theory of the structure and stability of atomic nuclei developed by Harkins and Wilson (1915) indicated that the elements with even atomic numbers should be more abundant than those with odd atomic numbers. The data supporting this rule were discussed by Harkins (1917), who found that the seven most abundant elements (O, Fe, Ni, Si, Mg, S, and Ca) in the meteorites, 443 of which were studied, are all even and that they make up 98.6 per cent of the meteoritic matter. The even-numbered elements were found to be in every case more abundant than the adjacent odd-numbered elements, and, on an average, the former were about seventy times as abundant as the latter. The same rule was found by Harkins to be valid also in the Earth's crust, although the evidence was poorer than in the meteorites, owing to the much more local character of the lithosphere. In any case, six of the first most abundant elements (O, Si, Fe, Ca, Mg, Ti) found therein are even and make up 85.74 per cent of the lithosphere, whereas the three odd elements (Al, Na, K) constitute only 12.77 per cent. In the upper lithosphere, hydrosphere, and atmosphere the even elements, on atomic percentage basis, are about ten times more abundant.

Figure 2.2 shows the general validity of the rule of Oddo and Harkins: The elements with even atomic number are nearly always more abundant than either of the two adjacent elements in the Periodic Table. According to Harkins (1931), in individual cases in which this is not true, the abundance of the element with even atomic number is greater than the arithmetic mean of the abundance of the two adjacent odd-numbered elements. The best illustration of the rule is

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supplied by elements which are geochemically coherent, i.e., those which are always found together in Nature. The best example of all is the group of the lanthanides. Their abundance relationships are presented in Figure 18.1.

The fact that the chemically and geochemically very coherent lanthanides follow the rule of Oddo and Harkins shows that this rule is no selection principle, but a true physical law. The most pronounced exceptions to the rule are found in the Earth's crust, where sodium ($Z = 11$) is more abundant than magnesium ($Z = 12$) and aluminum ($Z = 13$) likewise more abundant than magnesium. The abundance of phosphorus ($Z = 15$) is higher than that of sulfur ($Z = 16$). Moreover, manganese ($Z = 25$) is more abundant than chromium ($Z = 24$). Additional exceptions, even though less pronounced, are displayed by certain other elements in the upper lithosphere. As Harkins (1917) has already pointed out, certain groups of elements related in their physical and chemical properties are relatively more abundant in the upper lithosphere: sodium and potassium, the halogens, and aluminum are very much more abundant in the Earth's crust than in the meteorites. The said exceptions, according to Eskola (1946), afford a most important proof of the fact that the lithosphere has actually been formed by an extensive differentiation process.

THE ABUNDANCE AND STRUCTURE OF THE ATOMIC NUCLEUS

Abundance is related to the fundamental laws of nuclear forces. The cosmic abundance of nuclides is dominated by their stability and evolution. The abundance of the stable nuclides depends, even though in a very complicated manner, on the nuclear binding energy. In addition, the abundance depends on the number of particles associated with the nucleus, in particular on the sum of protons and neutrons (the mass number), and on the excess of neutrons in the nucleus. The abundance of a nonradioactive element also depends on the number of its stable isotopes. The importance of the mass number as a factor affecting the abundance is a result of the observation that the stability of the nuclides seems to be chiefly connected with their mass number. The notable differences which sometimes are observed between the abundance values of neighboring elements are caused by differences in nuclear binding energy.

The abundance calculations discussed previously deal only with the elements. With reference to their chemical properties the nu-

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clides constituting an element are closely, but not completely, alike. There are slight differences in the chemical behavior of the isotopes of an element, i.e., in the rate or extent to which certain chemical reactions take place. Such differences exist because the thermodynamic properties of the compounds of an element depend on the vibration frequency of the isotopic molecules. The vibration frequency, in turn, depends on the mass of the constituting atoms. In chemical reactions which take place in Nature, the isotopes of an element, owing to their different mass, may become separated from one another to a certain extent. It is evident that the abundance relationships of the elements are of prime importance for the geochemist, who studies his problem from a chemical point of view. However, the fact that the elements as such are not primary constituents, because they usually are composed of a number of different isotopes, necessitates the study of the abundance relationships of the nuclides. The detailed knowledge of the abundance of the nuclides will aid in understanding and deciphering the abundance relationships of the elements.

It must also be emphasized that the establishment of the abundance relationships of known nuclides, besides its importance in geochemistry, offers the nuclear physicist welcome experimental control of the theoretical calculations of the stability relationships of the nuclides. There exists between nuclear physics and geochemistry a contact zone in the abundance studies, and it is evident that here the two fields of study are able to contribute much to each other.

SOME CONCEPTS AND DEFINITIONS PERTAINING TO THE ATOMIC NUCLEUS

All nuclei are composed of positively charged protons and electrically neutral neutrons, both of which have masses approximately equaling one-sixteenth the mass of the oxygen atom. The number of protons in the nucleus is equal to the atomic number of the element in question in the Periodic Table. The letter Z is used to denote the proton number or the nuclear-charge number of the nucleus. On the other hand, the number of neutrons, N , or the neutron number, is independent of the atomic number. The mass number of the nucleus, A , is the sum of the number of protons and neutrons:

$$A = Z + N .$$

Therefore,

$$N = A - Z .$$

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Two of the three quantities, A , N , and Z , consequently, will unequivocally determine the third one. More than seven hundred nuclides are now known to exist. Most of them are radioactive and have been produced artificially.

Atoms of the same element all have the same atomic number, Z , but they may have different weights (mass numbers, A). They are called isotopes because they occupy the same position in the Periodic System. Atoms with the same mass number but with different atomic number are called isobars. Atoms with the same neutron number are called isotones. Examples of isobars, isotopes, and isotones are given in Table 2.6.

TABLE 2.6
EXAMPLES OF ISOBARS, ISOTOPES, AND ISOTONES

ELEMENT	ISOBARS $A=96$		ELEMENT	ISOTOPES $Z=44$		ELEMENT	ISOTONES $N=58$	
	Z	N		A	N		Z	A
Zr.....	40	56	Ru.....	96	52	Mo.....	42	100
Mo.....	42	54	Ru.....	98	54	Ru.....	44	102
Ru.....	44	52	Ru.....	99	55	Rh.....	45	103
			Ru.....	100	56	Pd.....	46	104
			Ru.....	101	57	Cd.....	48	106
			Ru.....	102	58			
			Ru.....	104	60			

In the abundance calculations presented in the previous paragraphs the proton number, Z , was used as a basis, and consequently the sum of the abundance of nuclides with the same atomic number was determined. Even though this manner of calculation is the most important one for general geochemical purposes, it characterizes the abundance only partially. From a nuclear-physical point of view the abundance calculations may as well be based on the mass number or on the neutron number, whereby the sum of the abundance of such nuclides will be given which have these numbers in common. A two-dimensional system of co-ordinates evidently does not suffice to give an unequivocal picture of the abundance of the nuclides. Only two of the three variables, A , N , and Z , do not depend on each other. Consequently, two independent co-ordinates would be necessary for the graphical presentation of the abundance, supplemented by a third co-ordinate expressing the abundance given in a suitable unit. However, the conventional way to express the abundance is to use

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a two-dimensional system of co-ordinates, as Goldschmidt (1937b) did; abundance is thereby always chosen as one of the co-ordinates, and the other co-ordinate represents, in turn, the proton, the mass, and the neutron number. With reference to the proton number, the abundance curve is presented in Figure 2.2. Consequently, it is necessary only to construct curves for the mass and neutron number. However, the abundance of the nuclides of the various elements will be discussed first.

ABUNDANCE OF THE NUCLIDES

All stable nuclides occur in Nature along with a number of unstable nuclides which have very long half-lives and their shorter-lived decay products. Radioactive decay and isotope fractionation cause changes in the abundance of the nuclides.

In order to calculate the absolute abundance of the various nuclides, the abundance of the elements and the relative abundance of their isotopes must be known. The facts pertaining to the elements have already been presented. The isotopic composition of the elements and the relative abundance of their isotopes are known. The relative abundance of the isotopes of stable and of the longest-lived unstable elements is given in Table 2.7, which is based mainly on the values given by Seaborg (1944).

Three rules, of high importance for the geochemist, characterize the nuclides presented in Table 2.7 and Figure 2.3. They are: (1) the symmetry rule, (2) the shell rule, and (3) the isobar rule.

The symmetry rule.—To a first approximation, the structure of the nuclei is symmetric in protons and neutrons. In stable nuclei with low atomic number the number of protons is approximately equal to that of neutrons. Consequently, their mass numbers are approximately twice the proton number. This ratio increases from 2 to 2.6 with increasing mass. This rule is illustrated by Figure 2.3, in which the disks and circles representing the various nuclides near the origin lie on both sides of the straight line that bisects the angle formed by the axes Z and N . With increasing mass number the points depart from the bisector more and more toward the N -axis. The explanation is that, when new protons and neutrons are added to the more simple nuclei, whose total charge is always positive, the electrically neutral neutron is incorporated into the nucleus more readily, because of the Coulomb repulsion between the positive proton and the nucleus.

The shell rule.—The facts presented in Table 2.7 show that all

TABLE 2.7
RELATIVE ABUNDANCE OF ISOTOPES OF STABLE AND OF
LONGEST-LIVED UNSTABLE ELEMENTS
(Unstable Isotopes Are Represented by *Italic A* Values)

<i>Z</i>	Element	Symbol	<i>N</i>	<i>A</i>	Relative Abundance (Per Cent)
0 . . .	Neutron	n	1	1	
1 .	Hydrogen Deuterium	H D	0 1	1 2	99.98 0.02
2	Helium	He	1 2	3 4	10 ⁻⁵ 100
3	Lithium	Li	3 4	6 7	7.5 92.5
4 . . .	Beryllium	Be	5	9	100.
5	Boron	B	5 6	10 11	18.83 81.17
6 . . .	Carbon	C	6 7	12 13	98.9 1.1
7 . .	Nitrogen	N	7 8	14 15	99.62 0.38
8 .	Oxygen	O	8 9 10	16 17 18	99.76 0.041 0.20
9 . . .	Fluorine	F	10	19	100.
10	Neon	Ne	10 11 12	20 21 22	90.00 0.27 9.73
11 . .	Sodium	Na	12	23	100
12.	Magnesium	Mg	12 13 14	24 25 26	77.4 11.5 11.1
13. . .	Aluminum	Al	14	27	100
14 . .	Silicon	Si	14 15 16	28 29 30	92.28 4.67 3.05
15 . .	Phosphorus	P	16	31	100.
16 . .	Sulfur	S	16 17 18 20	32 33 34 36	95.1 0.74 4.2 0.016
17. . . .	Chlorine	Cl	18 20	35 37	75.4 24.6

TABLE 2.7—*Continued*

<i>Z</i>	Element	Symbol	<i>N</i>	<i>A</i>	Relative Abundance (Per Cent)
18	Argon	A	18	36	0 307
			20	38	0 061
			22	40	99 632
19	Potassium	K	20	39	93 38
			21	40	0 012
			22	41	6 61
20	Calcium	Ca	20	40	96 96
			22	42	0 64
			23	43	0 15
			24	44	2 06
			26	46	0 0033
			28	48	0 19
21	Scandium	Sc	24	45	100.
22	Titanium	Ti	24	46	7 95
			25	47	7 75
			26	48	73.45
			27	49	5 51
			28	50	5.34
23	Vanadium	V	28	51	100.
24	Chromium	Cr	26	50	4 49
			28	52	83 78
			29	53	9 43
			30	54	2 30
25	Manganese	Mn	30	55	100
26	Iron	Fe	28	54	6 04
			30	56	91 57
			31	57	2 11
			32	58	0 28
27	Cobalt	Co	32	59	100.
28	Nickel	Ni	30	58	67 4
			32	60	26 7
			33	61	1 2
			34	62	3 8
			36	64	0 88
29	Copper	Cu	34	63	70 13
			36	65	29 87
30	Zinc	Zn	34	64	50 9
			36	66	27 3
			37	67	3.9
			38	68	17 4
			40	70	0 5
31	Gallium	Ga	38	69	61 2
			40	71	38.8

TABLE 2.7—Continued

<i>Z</i>	Element	Symbol	<i>N</i>	<i>A</i>	Relative Abundance (Per Cent)
32.	Germanium	Ge	38	70	21.2
			40	72	27.3
			41	73	7.9
			42	74	37.1
			44	76	6.5
33	Arsenic	As	42	75	100.
34 . .	Selenium	Se	40	74	0.9
			42	76	9.5
			43	77	8.3
			44	78	24.0
			46	80	48.0
			48	82	9.3
35 . . .	Bromine	Br	44	79	50.6
			46	81	49.4
36. . . .	Krypton	Kr	42	78	0.35
			44	80	2.01
			46	82	11.53
			47	83	11.53
			48	84	57.11
			50	86	17.47
37	Rubidium	Rb	48	85	72.8
			50	87	27.2
38 . .	Strontium	Sr	46	84	0.56
			48	86	9.86
			49	87	7.02
			50	88	82.56
39. . . .	Yttrium	Y	50	89	100.
40 . . .	Zirconium	Zr	50	90	48.
			51	91	11.5
			52	92	22.
			54	94	17.
			56	96	1.5
41	Columbium	Cb	52	93	100.
42 .	Molybdenum	Mo	50	92	14.9
			52	94	9.4
			53	95	16.1
			54	96	16.6
			55	97	9.65
			56	98	24.1
			58	100	9.25
43	Technetium	Tc	56	99	
44	Ruthenium	Ru	52	96	5.68
			54	98	2.22
			55	99	12.81
			56	100	12.70
			57	101	16.98
			58	102	31.34
			60	104	18.27

TABLE 2.7—Continued

<i>Z</i>	Element	Symbol	<i>N</i>	<i>A</i>	Relative Abundance (Per Cent)
45	Rhodium	Rh	58	103	100.
46	Palladium	Pd	56 58 59 60 62 64	102 104 105 106 108 110	0.8 9.3 22.6 27.2 26.8 13.5
47	Silver	Ag	60 62	107 109	51.9 48.1
48	Cadmium	Cd	58 60 62 63 64 65 66 68	106 108 110 111 112 113 114 116	1.4 1.0 12.8 13.0 24.2 12.3 28.0 7.3
49	Indium	In	64 66	113 115	4.5 95.5
50	Tin	Sn	62 64 65 66 67 68 69 70 72 74	112 114 115 116 117 118 119 120 122 124	1.1 0.8 0.4 15.5 9.1 22.5 9.8 28.5 5.5 6.8
51	Antimony	Sb	70 72	121 123	56. 44.
52	Tellurium	Te	68 70 71 72 73 74 76 78	120 122 123 124 125 126 128 130	0.088 2.43 0.85 4.59 6.93 18.71 31.86 34.52
53	Iodine	I	74	127	100.
54	Xenon	Xe	70 72 74 75 76 77 78 80 82	124 126 128 129 130 131 132 134 136	0.094 0.088 1.90 26.23 4.07 21.17 26.96 10.54 8.95
55	Cesium	Cs	78	133	100.

TABLE 2.7—Continued

Z	Element	Symbol	N	A	Relative Abundance (Per Cent)
56	Barium	Ba	74	130	0 101
			76	132	0 097
			78	134	2 42
			79	135	6 59
			80	136	7 81
			81	137	11 32
			82	138	71 66
57 .	Lanthanum	La	82	139	100
58 ..	Cerium	Ce	82	140	89.
			84	142	11
59 ...	Praseodymium	Pr	82	141	100
60	Neodymium	Nd	82	142	25 95
			83	143	13 0
			84	144	22 6
			85	145	9 2
			86	146	16 5
			88	148	6 8
			90	150	5 95
61. . .	Promethium	Pm	86	147	
62. ..	Samarium	Sm	82	144	3.
			85	147	17.
			86	148	14.
			87	149	15.
			88	150	5.
			90	152	26
			92	154	20.
63. ...	Europium	Eu	88	151	49.1
			90	153	50.9
64. . . .	Gadolinium	Gd	88	152	0 2
			90	154	2 86
			91	155	15 61
			92	156	20 59
			93	157	16 42
			94	158	23 45
			96	160	20.87
65 .	Terbium	Tb	94	159	100.
66.	Dysprosium	Dy	92	158	0 1
			94	160	1.5
			95	161	22.
			96	162	24.
			97	163	24.
			98	164	28.
67	Holmium	Ho	98	165	100.
68.	Erbium	Er	94	162	0 1
			96	164	1 5
			98	166	32 9
			99	167	24 4
			100	168	26 9
			102	170	14 2
69.	Thulium	Tm	100	169	100.

TABLE 2.7—Continued

<i>Z</i>	Element	Symbol	<i>N</i>	<i>A</i>	Relative Abundance (Per Cent)
70 .	Ytterbium	Yb	98	168	0.06
			100	170	4.21
			101	171	14.26
			102	172	21.49
			103	173	17.02
			104	174	29.58
			106	176	13.38
71 .	Lutecium	Lu	104	175	97.5
			105	176	2.5
72	Hafnium	Hf	102	174	0.18
			104	176	5.30
			105	177	18.47
			106	178	27.13
			107	179	13.85
			108	180	35.14
73 . .	Tantalum	Ta	108	181	100.
74	Tungsten	W	106	180	0.122
			108	182	25.80
			109	183	14.26
			110	184	30.74
			112	186	29.22
75	Rhenium	Re	110	185	38.2
			112	187	61.8
76	Osmium	Os	108	184	0.018
			110	186	1.59
			111	187	1.64
			112	188	13.3
			113	189	16.1
			114	190	26.4
			116	192	41.0
77. . . .	Iridium	Ir	114	191	38.5
			116	193	61.5
78	Platinum	Pt	114	192	0.8
			116	194	30.2
			117	195	35.3
			118	196	26.6
			120	198	7.2
79	Gold	Au	118	197	100
80	Mercury	Hg	116	196	0.15
			118	198	10.1
			119	199	17.0
			120	200	23.3
			121	201	13.2
			122	202	29.6
			124	204	6.7
81.	Thallium	Tl	122	203	29.1
			124	205	70.9
82.	Lead	Pb	122	204	1.5
			124	206	23.6
			125	207	22.6
			126	208	52.3

TABLE 2.7—Continued

<i>Z</i>	Element	Symbol	<i>N</i>	<i>A</i>	Relative Abundance (Per Cent)
83	Bismuth	Bi	126	209	100 .
84	Polonium	Po	126	210	
85	Astatine	At	126	211	
86	Radon	Rn	136	222	
87	Francium	Fa	136	223	
88	Radium	Ra	138	226	
89	Actinium	Ac	138	227	
90	Thorium	Th	142	232	100 .
91	Protactinium	Pa	140	231	
92	Uranium	U	142 143 146	234 235 238	0 .006 0 .71 99 .28
93	Neptunium	Np	144 146	237 239	
94	Plutonium	Pu	144 145	238 239	
95	Americium	Am	146	241	
96	Curium	Cm	146	242	

known nuclei may be divided into four groups, depending on whether they have even (*e*) or odd (*o*) atomic (proton) and neutron numbers, the types being the following:²

Type	Example
(<i>e</i> - <i>e</i>)	${}_8\text{O}^{16}$
(<i>e</i> - <i>o</i>)	${}_4\text{Be}^9$
(<i>o</i> - <i>e</i>)	${}_3\text{Li}^7$
(<i>o</i> - <i>o</i>)	${}_5\text{B}^{10}$

Protons and neutrons form shells of two in the nuclei. If an odd proton or neutron is added to a nucleus which possesses only closed

2. The nuclides are unequivocally indicated by using *Z* and *A* as subscript and superscript, respectively. The atomic number is usually written as a left subscript to the symbol, and the mass number is used as a right superscript. Thus ${}_{92}\text{U}^{235}$ designates the uranium atom with the atomic number 92 and the mass number 235. According to the equation $N = A - Z$, its neutron number equals $235 - 92$, or 143. As a subscript, *Z* may also be neglected altogether, whereby the designation becomes U^{235} . In the symbols of the types, the character of the proton number is given first, followed by the character of the neutron number. Thus, e.g., (*e* - *o*) means that the proton number is even and the neutron number odd; it follows that the mass number is odd.

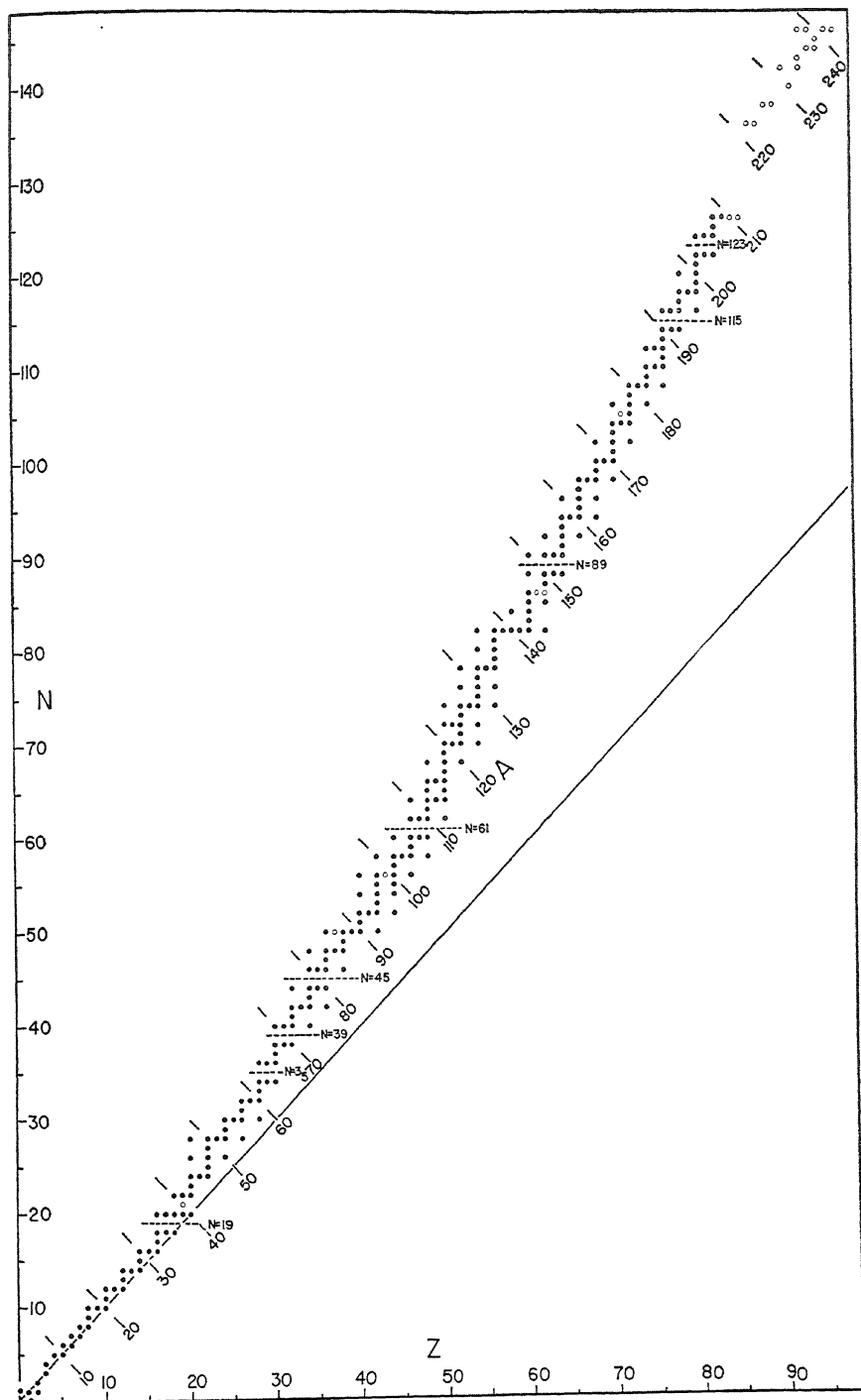


FIG. 2.3.—The stable (•) and the longest-lived unstable (o) nuclides

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shells, e.g., of the type $(e - e)$, in which the number both of protons and of neutrons is even, the bond between this particle and the nucleus is relatively weak. In other words, the new nucleus is less stable than the previous one. Consequently, the nuclides of the type $(e - e)$ are more strongly bound than those with unclosed shells, such as nuclei of the types $(e - o)$ and $(o - e)$, whereas the type $(o - o)$ is still less stable. According to the shell rule, the type $(e - e)$ is the most common of the nuclides found in Nature, whereas the type $(o - o)$ is very rare. The types $(e - o)$ and $(o - e)$ are about equally abundant. The 295 nuclides presented in Table 2.7 (272 stable and 23 unstable nuclides; eight of the unstable nuclides have very long half-lives and three of the eight have long chains of shorter-lived descendants) are distributed among the various types in the following way:

Type	No. of Nuclides
$(e - e)$	169
$(e - o)$	58
$(o - e)$	62
$(o - o)$	6

This distribution shows that the nuclides with even neutron number preponderate over those with odd neutron number. Also the proton number is usually even.

The four light stable nuclei of the type $(o - o)$ are D^2 , Li^6 , B^{10} , and N^{14} . The β -active K^{40} and Lu^{176} also belong to this type. The facts presented in Table 2.7 further show that in elements with even atomic number the nuclei of the type $(e - e)$ are more abundant than those of the type $(e - o)$. Among the six elements with odd atomic number and an $(o - o)$ -type nucleus, only for nitrogen the $(o - o)$ nucleus is more abundant than the other nucleus of the type $(o - e)$. In the case of the other five elements the type $(o - e)$ is the most abundant one.

If an odd element with $Z = 2n + 1$ is considered, it is evident that its isotopes can belong only to the types $(o - e)$ and $(o - o)$. The most stable and the most abundant type, $(e - e)$, is thus out of the question, and therefore it follows that the absolute abundance of elements with even atomic number is greater than the abundance of odd-numbered elements. This is the explanation of the rule of Oddo and Harkins, and it was already predicted by Harkins in 1917. There occur strong individual fluctuations from element to element; but as a general rule the even elements are about ten times as abun-

dant as their odd-numbered neighbors in the upper lithosphere, and the factor is 50 for the meteorites and 10 for the solar atmosphere (Harkins, 1931). The absolute abundance decreases from element to element, on an average, by a factor of 1.2–1.3. Consequently, the heaviest stable elements ($Z = 83$) are rarer than the lightest by the factor $(1.2)^{83}$ or approximately 10^7 (Fluegge, 1946). Next to the rule of Oddo and Harkins, the decreasing abundance with increasing atomic number is the most important rule governing the abundance relationships of the elements. According to Goldschmidt (1926, 1930a), the abundance in general, to a first approximation, is inversely proportional to the seventh or eighth power of the proton number. This regularity is graphically illustrated by the fact that the points representing the logarithm of the abundance of the elements as a function of the logarithm of the proton number fall on a narrow strip bounded by two approximately straight lines which represent the abundance of the even- and odd-numbered elements, respectively. Elements rising above this strip are called abundant elements, e.g., iron and nickel, whereas those falling below are called deficient elements, e.g., lithium, beryllium, and boron.

The isobar rule.—This rule is wholly empirical and, so far, lacks theoretical basis. It indicates the presence or absence of nuclides of equal mass (isobars). The following principles are valid according to the isobar rule.

1. The difference of the proton numbers of two stable isobars is greater than 1 (Mattauch's rule; Mattauch, 1934a, b). In other words, there exist no stable pairs of isobars whose proton numbers differ by only one unit; that is, stable isobars of neighboring elements do not exist. The exceptions to Mattauch's rule are the following pairs: $\text{Cd}^{113}\text{-In}^{113}$; $\text{In}^{115}\text{-Sn}^{115}$; $\text{Sb}^{123}\text{-Te}^{123}$; $\text{Re}^{187}\text{-Os}^{187}$. However, these four exceptions are, perhaps, not real, and it is probable that the second-named nuclides in these pairs are unstable and go slowly over into the former ones (Mattauch, 1937). If these nuclides are stable, the rule must be modified to state that the number of isobars with odd mass number tends to be small.

2. If the mass number is even, the proton and neutron numbers are also even. Consequently, the type ($o - o$) should be forbidden altogether. As a matter of fact, only four representatives of this type among the lightest nuclides are known, viz., ${}_1\text{D}^2$, ${}_3\text{Li}^6$, ${}_5\text{B}^{10}$, and ${}_7\text{N}^{14}$. The explanation is that strong individual fluctuations still are possible in the lightest nuclides.

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3. Each of the nuclei of the types $(e - o)$ and $(o - e)$, which have odd mass number, is represented by only one isobar. This isobar is the energetically most favorable one; the other isobars are unstable (β -active). In other words, there exist no isobars with odd mass number. There are no exceptions to this rule. On the other hand, the nuclides of the type $(e - e)$ usually possess two, sometimes three, stable isobars.

The three rules presented above explain many observations dealing with the existence and abundance of the various nuclides. It was pointed out previously that there is a drop in the atomic abundance curve at the place of nickel (see Fig. 2.2). A corresponding jump occurs in the isotopic composition of the elements at the same place in the Periodic System, i.e., at $Z = 28$.

Table 2.7 shows that the elements with odd atomic number have, as a rule, only one or two stable isotopes (Aston's rule). The even-numbered elements, in general, have a considerably higher number of isotopes than do the odd elements. In addition, the lighter of the two isotopes of an element with odd atomic number is usually the more abundant (Harkins, 1931). The exceptions to this rule consist of the elements Li, B, In, Eu, Re, Ir, and Tl.

In elements with Z less than 28, one of the isotopes usually predominates, and the percentage of the other isotopes is commonly rather low. Only for boron and chlorine is the latter percentage higher, viz., 18.83 and 24.6, respectively. Starting with nickel, however, the isotopes tend to become more evenly distributed, and often two or three isotopes are present in nearly equal percentages; a chief isotope exists in comparatively few elements. The number of the isotopes also changes rather abruptly. Below $Z = 28$ the even-numbered elements seldom have more than three or four isotopes, only calcium and titanium being exceptions to this rule; but starting with $Z = 28$ the isotopes grow more numerous until, at $Z = 81$, their number again decreases, and, starting with $Z = 83$, most of the remaining elements have only one isotope.

An empirical rule states that for an element the abundance of stable isotopes with even mass number as a function of the mass has only one maximum. The lightest isotopes of a number of elements form an exception to this rule. The abundance of the heaviest isotopes of calcium and tin and that of the isotopes of samarium are also exceptional.

Another empirical rule established by Mattauch (1937) states that

ABUNDANCE OF ELEMENTS AND NUCLIDES

the elements possess only one or two stable isotopes with odd mass number. If there are two such isotopes, they are of practically equal abundance. The abundance ratio is never less than 1:0.4, whereas the abundance of isotopes with even mass number may differ by several powers of 10. The following nuclides form exceptions to this rule: Cl^{35} , K^{39} , Rb^{87} , In^{113} , Sn^{115} , Te^{123} , and Os^{187} . It should be noticed that the last four nuclides are the exceptions to Mattauch's rule as well.

The abrupt changes which take place at the triad Fe-Co-Ni show that a corresponding change in the structure of the atomic nucleus evidently occurs here. Such changes also require special consideration when the abundance relationships are dealt with. The high abundance of iron is probably related to the fact that the packing energy of the atom is at its maximum here.

As was pointed out previously, the abundance of the nuclides, in general, might be expected to depend directly on the nuclear binding energy, provided that the nuclides are assumed to have been formed at temperatures high enough to allow the establishment of thermal equilibrium between the nuclei and their free constituents. The dependence should be such that the most abundant nuclei are the most stable. The discussion on the preceding pages shows that this relationship actually is very clearly found empirically.

ABUNDANCE CALCULATIONS BASED ON THE MASS NUMBER

The sum of the abundance values for isobars has been calculated by Goldschmidt (1937*b*). A graph showing the course of abundance is presented in Figure 2.4, which is redrawn from Goldschmidt's paper.

As was pointed out in a previous paragraph, very close relationships exist between the abundance and the mass number of the nuclides. It may be concluded from the shell rule that the rule of Oddo and Harkins is valid also with reference to mass number, that is, nuclides with even mass number are more abundant than the neighboring nuclides with odd mass number. Moreover, the sum of the cosmic abundance of isobars with even mass number is always greater than the sum of the cosmic abundance of the neighboring isobars with odd mass number. The difference of the abundance sums decreases with increasing mass number. This is the universal nuclear physical form of the rule of Oddo and Harkins (Suess, 1947*a*).

Like the rule of Oddo and Harkins, other features peculiar to the

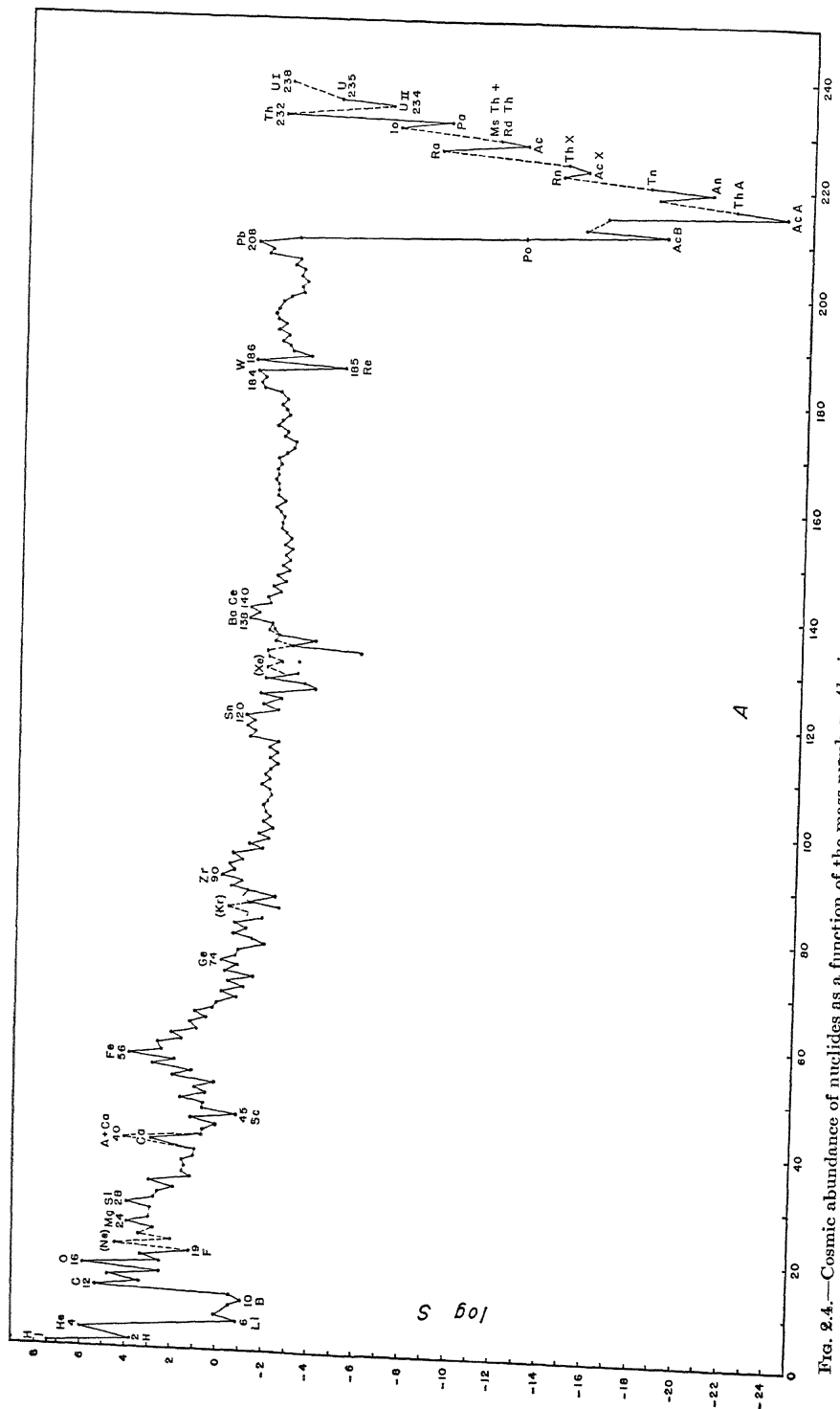


Fig. 2.4.—Cosmic abundance of nuclides as a function of the mass number. *Abscissa*, mass number (A). *Ordinate*, logarithm of the abundance ($\log S$)

ABUNDANCE OF ELEMENTS AND NUCLIDES

abundance curve based on proton number are displayed also by the curve based on mass number. Consequently, there is an abrupt drop in the abundance curve which sets in at the mass number 56, one of the isotopes of iron. At the mass numbers belonging to lithium, beryllium, and boron the abundance curve passes through a deep minimum. A feature characteristic of the A -log S curve is that nuclides with mass numbers which are integral multiples of 4 dominate up to a mass number of about 60.

Clarke (1889) was the first to draw an abundance curve for the elements. He took the atomic weight for one set of co-ordinates. Clarke expressly stated that all the abundant elements are low in the scale of atomic weights, reaching a maximum at 56 in iron. Above 56 the elements are comparatively rare, and only two of them, strontium and barium, appeared in Clarke's estimates. Another regularity which Clarke observed was the decrease of abundance with increasing atomic weight in several groups of the elements, e.g., in the alkali metals.

Suess (1947a) formulated a number of general rules for the cosmic abundance of the elements as a function of the mass number. These rules, which are generalizations of some of the empirical abundance rules presented in the previous paragraphs, follow.

1. The abundance of nuclides with odd mass number changes steadily with the mass. The nuclides which have neighboring isobars form exceptions to this rule: Sr^{87} , In^{113} , Sn^{115} , Te^{123} , and Os^{187} . In these cases, when two isobars exist for one mass number, the sum of the abundance of the isobars changes steadily with the mass.

2. The abundance of nuclides with even mass number and with similar neutron excess ($N - Z$) changes steadily with the mass. The generalized rule is that the points representing the abundance of nuclides with even mass number in a three-dimensional N - Z -log S diagram lie on a steady surface. However, there are numerous exceptions to these rules among the intermediate nuclides. In addition, in every series of the intermediate nuclides with equal neutron excess the heaviest nuclide is more abundant than the rule requires.

3. For the intermediate and heavy nuclides of both even and odd mass number the following rule is valid: For each mass number the isobar with the lowest neutron excess is the least abundant. Above $A = 70$ there are only four exceptions to this rule, viz., at the mass numbers 76, 110, 116, and 142.

Using these plausible abundance rules, which agree with nuclear

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physical facts, Suess (1947a) calculated new modified cosmic abundance values for heavy and intermediate elements. Goldschmidt's (1937b) values for the ferrides and the lanthanides served as the basis of the new values for the other elements. The adjusted values agree well with the known facts on the isotopic constitution of the elements, even though they are still preliminary. According to Suess (1947b), the new abundance values show that the following elements are notably deficient in the meteorites, as compared with other cosmic sources: S, Se, Te; Ga, In, Tl; Zn, Cd, Hg; Re. It must be noticed that the elements in each of the three groups are chemically similar. Their deficiency is probably caused by secondary chemical processes.

The new abundance values, presented by a graph, show very clearly the prominence of nuclides with certain proton and neutron numbers (so-called magic numbers). Certain neutron excess values are also prominent, even though less pronouncedly so. According to Goldschmidt (1937b) and Suess (1947b), the nuclides with an N of 20, 28, 50, and 82 and those with a Z of 28, 50, 74, and 82 are cosmically very abundant. In like manner, nuclides with a neutron excess of 4, 12, 24, and 26 are more abundant than other nuclides (Suess, 1947b).

ABUNDANCE CALCULATIONS BASED ON THE NEUTRON NUMBER

The abundance of the isotones was also calculated by Goldschmidt (1937b). The corresponding abundance graph, according to his paper, is presented in Figure 2.5, which gives the sum of the abundance of all nuclides having the same neutron number. The regularities shown by the two abundance graphs already presented are generally revealed also by the isotonic abundance curve.

NUCLIDES NOT FOUND IN NATURE

Beginning with the discovery of the law of periodicity by D. Mendeleev and Lothar Meyer in 1869, the elements have been subjects of intensive research, with the ultimate aim of the completion of the Periodic System. Sixty-three elements were known in 1870, and after the discovery of hafnium by D. Coster and G. Hevesy in 1923 and the discovery of rhenium by W. Noddack, Ida Tacke (Noddack), and O. Berg in 1925, only the elements with the atomic numbers 43, 61, 85, and 87 still remained undiscovered. Although it must now be assumed that the elements 43 (technetium) and 61 (promethium)³

3. The name promethium is adopted for the element 61 in this book, but the naming of this element is still unsettled.

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do not occur in Nature, all these elements have been artificially prepared and their properties studied (see chap. 46).

When the Periodic Law was discovered, the modern experimental study of the atomic nucleus and its structure was not even dreamed of. Still, after the discovery of the isotopes in 1913 and the substitution of the physical atomic numbers for the chemical atomic weights, the absence of some elements with certain atomic numbers in the Periodic System was not theoretically understood but was first credited to the inadequate knowledge of the chemical composition of

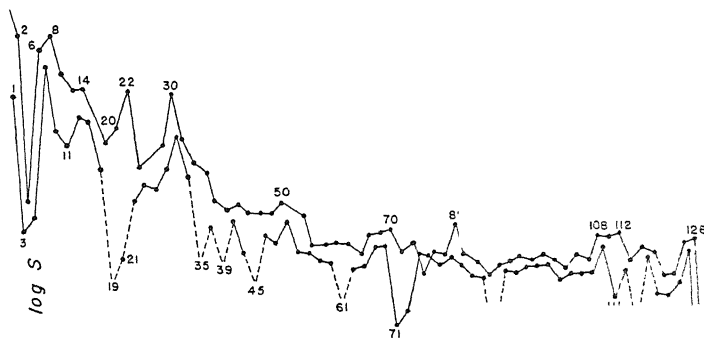


FIG. 2.5.—Cosmic abundance of nuclides as a function of the neutron number. *Abscissa*, neutron number (N). *Ordinate*, logarithm of the abundance ($\log S$).

rocks and minerals. Notwithstanding the increasing knowledge of the manner of occurrence of the elements and the use of new and improved methods of investigation, the four elements referred to above, however, still were not discovered in Nature.

As Figure 2.3 shows, the absence of certain proton numbers in the natural system of the nuclides is a fact no more surprising than, e.g., the absence of some neutron numbers. The neutron numbers 19, 35, 39, 45, 61, 89, 115, and 123 are unknown among the stable nuclides which occur in Nature, and the mass numbers 5 and 8 are absent as well. Because these neutron and mass numbers do not represent any given species of the elements, their absence is not so striking as is the absence of certain proton numbers. However, from a nuclear-physical viewpoint, the proton, neutron, and mass numbers are of equal im-

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portance. From this point of view it is not necessary that all proton numbers, e.g., from 1 to 83, must be represented by stable elements.

With special reference to the elements technetium ($Z = 43$) and promethium ($Z = 61$), it should be noticed that they have odd proton numbers and consequently can belong only to the types ($o - e$) and ($o - o$). However, according to the isobar rule, the type ($o - o$) seems to be excluded. According to Table 2.7, all mass numbers conceivable, which must necessarily be odd, are already occupied by nuclides belonging to the following elements:

Z	A	Z	A
43	95 Mo	61	143 Nd
	97 Mo		145 Nd
	99 Ru		147 Sm
	101 Ru		149 Sm
	103 Rh		

According to the isobar rule, each odd mass number cannot be represented by more than one stable nuclide, and consequently no stable nuclides are left at the disposal of technetium and promethium. The conclusion follows that, even though there is place in the Periodic System for these elements, this seems not to be the case in the system of the stable nuclides. Although the isobar rule is entirely empirical and valid only for the stable nuclides, the possibility is ruled out that isotopes of technetium and promethium could occur in Nature if their half-lives were long enough to validate their presence.

The elements with $Z = 85$ (astatine) and $Z = 87$ (francium) are now known to occur in Nature in the form of very short-lived radioactive isotopes (see chap. 46).

ORIGIN OF THE ABUNDANCE DISTRIBUTION OF THE ELEMENTS

The calculations dealing with the cosmic abundance of the elements pose the problem of whether the observed abundance relationships are merely accidental or whether they may be explained on the basis of known physical laws. As was pointed out in a previous paragraph, the abundance of an element is related to nuclear stability. As early as 1917, W. D. Harkins considered the preponderance of elements with a low atomic number to be a probable result of the evolution of the elements.

The information available on atom-building processes shows that very probably the present abundance relationships of the nuclides

ABUNDANCE OF ELEMENTS AND NUCLIDES

are caused by two factors. First, the abundance of the nuclides depends on the circumstances under which the nuclei were originally formed. Second, it is probable that at least a partial equilibrium is maintained between the various nuclides, determined by their stability relationships.

It is now generally believed that the elements cannot form under conditions assumed to exist in the interiors of the stars. Consequently, it is believed that the elements were synthesized and their abundance relationships established in an early stage of the evolution of the Universe. Since 1931, frequent attempts have been made to interpret the present abundance distribution of the elements as a result of a "frozen" thermodynamic equilibrium state between the atom-building and the disintegrating processes, which was determined by the nuclear binding energy of the elements and which corresponded to the very high temperatures, pressures, and densities supposed to have existed during the early stages of the expansion of the Universe. It is believed that under such physical conditions appreciable rates of nuclear transformation were permitted for both light and heavy nuclides. Under the assumption of temperatures of the order of 10^{10} – 10^{11} degrees, pressures of the order of 10^{19} – 10^{27} atm, and densities of the order of 10^7 – 10^{13} g·cm⁻³, v. Weizsäcker (1938) and Chandrasekhar and Henrich (1942) explained the observed cosmic abundance of nuclides from O¹⁶ upward. Chandrasekhar and Henrich assumed that the heavy elements were formed first and that their abundance was already frozen when the formation of the lighter elements started.

The pronounced dependence of the abundance, taken as a whole, on the neutron excess suggests, according to Suess (1947a), that the elements must have formed from a source with a very high neutron density, which greatly exceeded the proton density. The observed cosmic abundance of the elements shows that the present abundance distribution is the result of a thermodynamic equilibrium, which, however, was only rough and approximate and was disturbed in many details. However, according to Gamow (1946, 1948a, b), the slope of the abundance curve does not favor the hypothesis of the frozen equilibrium, because, according to the equilibrium theory, the logarithm of the abundance must be a linear function of the nuclear binding energy, which is a linear function of mass number. Therefore, one would expect a rapid exponential decrease of the abundance toward the heavy nuclides. Actually, the abundance of the light and

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the first half of the intermediate nuclides decreases rather rapidly, whereas the abundance of the heavier nuclides, from silver onward, remains nearly constant. To explain this discrepancy, Gamow assumed that the nuclides were not formed as a result of a frozen equilibrium state but rather in a continuous, unfinished building-up process from a highly compressed overheated neutron gas, which decayed into protons and electrons. The conditions necessary for rapid nuclear reactions were of very short duration, and probably no equilibrium could be established during this period. The neutrons formed complexes which later were converted into various nuclides of increasing complexity.

Unsöld (1948*a*) also found the hypothesis of an initial frozen nuclear equilibrium untenable and suggested that few other nuclides than the heavy ones were formed in the beginning and that they were decomposed in a later stage of the evolution. The abundance of the resulting lighter nuclides corresponds roughly to a thermal equilibrium, which, however, froze promptly with the decay of the heavy nuclides.

It must be noticed that the hypotheses presented above and other discussions of similar character are based largely on the cosmic-abundance values of the elements as given by Goldschmidt (1937*b*). However, as Suess (1947*b*) showed, many of the abundance values are uncertain and must be replaced by new values. Consequently, the final evaluation of the hypotheses must wait until new accurate abundance data are available.

It is generally assumed that the elements of a large part or of the whole of the Universe were created during a momentary, catastrophic happening. Present-day evidence indicates that the elements were created no more than $5 \cdot 10^9$ years ago (Unsöld, 1948*a*). However, Unsöld suggested that certain main-sequence stars are younger than the rest of the Galaxy and may still form today. Therefore, elements may also form, even now, in masses of the order of magnitude of a star in an early stage of stellar evolution.

It is assumed that, when the elements were formed, all possible nuclides were created. Among the radioactive nuclides, the short-lived and intermediate-lived ones have since decayed, leaving only the nuclides with a half-life of the same order of magnitude as the total of astronomical and geological time. The abundance relationships and the isotope ratios, once created, have remained rather stable, with the exception of the light elements, whose abundance has changed in the thermonuclear processes taking place in the stellar

ABUNDANCE OF ELEMENTS AND NUCLIDES

interiors. Radioactive decay and probably also nuclear fission have modified the primary cosmic abundance of the nuclides. In addition, if limited parts of the Universe, such as the planets, are considered, both the relative and the absolute abundance of the elements is found to have suffered changes in many cases, owing to differentiation in a gravitational field, diffusion, and a number of chemical processes. Consequently, with reference to the upper lithosphere, not all present-day abundance values of the nuclides are identical with the values valid at the time of the solidification of the Earth's crust.

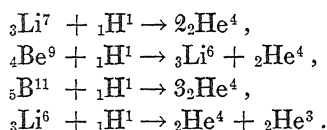
ABUNDANCE AND NUCLEAR TRANSMUTATION

The fundamental particles (protons, neutrons, and electrons), other elementary particles (deuteron, α -particles), and γ -rays are effective in inducing nuclear transmutation processes. The particles may be accelerated thermally or released in nuclear reactions. The nuclear transmutation has caused and still continues to cause definite changes in the abundance of the elements in Nature. Moreover, artificial transmutation has produced many isotopes of the missing elements of the Periodic System, along with a number of man-made elements—the transuranium elements (see chap. 46).

Geochemically, the most important nuclear transmutations are the ones which cause the scarcity of lithium, beryllium, and boron and the high cosmic abundance of helium. As pointed out previously, all abundance graphs show a pronounced minimum at the places belonging to lithium, beryllium, and boron. The deficiency of these elements in the upper lithosphere cannot be the result of any chemical selection principle because they are strongly lithophile and, moreover, become concentrated in the residual magmatic solutions of low density. Therefore, they actually should be rather abundant in the upper lithosphere. Goldschmidt (1926) predicted that the remarkable scarcity of the three elements must depend on their atomic structure, the cause of their deficiency being either the low probability of their formation or their instability. Goldschmidt's prediction was fulfilled when Atkinson and Houtermans (1929) showed theoretically that these elements are unstable and that they are relatively easily disintegrated if bombarded with fast-moving, thermally accelerated protons. They suggested that, at the high temperatures and pressures prevailing in stellar interiors, the light nuclei, if bombarded with protons, were readily built up into heavier nuclei. The theoretical rate of penetration falls off rapidly with increasing proton number; this explains the rise from the minimum. Consequently, this process

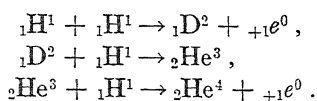
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is not possible for the heavy nuclei. Cockcroft and Walton (1930, 1932) confirmed this theory experimentally by accomplishing the first successful transmutation induced by energetic protons: they bombarded lithium with protons. Alpha particles were emitted from lithium during the bombardment when the atoms broke apart. Helium was thus produced as the result of the bombardment. In some cases a heavier atom results from the collision under the emission of a proton or a neutron. The disintegration reactions in question are the following:



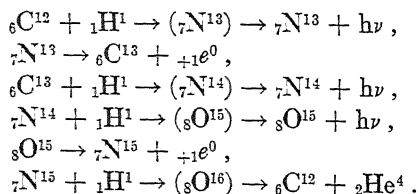
Consequently, atoms of these three elements are transformed into other atoms in the stellar interiors, and only a few are left. This fact accounts for their scarcity in the Universe.

Nuclear transmutations are believed to be the main source of stellar energy. According to astrophysical evidence, protons are the most abundant nuclei in stars of the main sequence. It was therefore suggested (Bethe, 1939) that the production of stellar energy was entirely due to thermonuclear reactions involving the constant transmutation of protons into helium nuclei. Helium, in spite of its high abundance, does not react with protons because the product, He^5 , does not exist. In the fainter stars with lower central temperature the following cycle is the most probable because it depends less on temperature:



However, this process is still incompletely understood in astronomical and nuclear-physical respects.

For stars of the main sequence which are more massive than the Sun, the chain of reactions, found independently by v. Weizsäcker (1938) and Bethe (1938), is:



ABUNDANCE OF ELEMENTS AND NUCLIDES

In these cycles four protons and two electrons are combined into an α -particle (helium nucleus), and carbon and nitrogen act as true catalysts, which are reproduced practically completely. Consequently, their abundance remains unchanged. The carbon-nitrogen reactions occurring in the stars are unique in their cyclical character. No nuclei heavier than He^4 can be built up permanently in ordinary stars, except in negligible amounts, because all nonradioactive nuclei lighter than carbon, with the exception of H^1 and He^4 , have extremely short lives in the stellar interiors. Consequently, such elements may be present only to the extent to which they are continuously generated in nuclear reactions from longer-lived elements. This is in accord with their low terrestrial and cosmic abundance. They are disintegrated by proton bombardment, under the emission of an α -particle, whereby the original nucleus is permanently destroyed. This, again, explains the low abundance of lithium, beryllium, and boron, which would "burn" in a very short time and which, unlike carbon, cannot be replaced in the cycle. The elements heavier than carbon and nitrogen react too slowly and are consequently of no importance in energy production. For all elements heavier than fluorine there occurs only radiative capture of protons, whereby the original nucleus is destroyed. In the case of oxygen and fluorine the reactions usually lead back to nitrogen.

In the transformation of hydrogen into helium, hydrogen is the fuel and helium the slag. The two reaction chains account for the high cosmic abundance of helium. However, it is probable that many stars also contain original helium.

GEOCHEMICAL STRUCTURE OF THE EARTH

INTRODUCTORY REMARKS

AS WAS emphasized in chapter 1, meteorites, representing the only existing rocks outside the Earth's outer crust, are of outstanding importance for the study of the chemical composition of the Earth's interior. Since the French scientist, A. Boisse, in 1850 suggested for the first time that the bulk composition of the Earth is comparable with the average composition of meteorites, the possible similarity of the Earth and the meteorites has been widely discussed by scientists in all fields connected with the question.

Interest in the analogy between the Earth and meteorites has been revived by the recent work of Brown and Patterson (1947*a, b*; 1948). As mentioned in chapter 1, these authors have arrived at the conclusion that various meteoritic materials represent different equilibrium compositions. The temperature and pressure at which equilibrium has been achieved in a meteorite are higher, the greater the amount of the metal phase. There is as yet no final proof that meteorites originate from a single parent-planet. It does seem very likely, however, that meteorites represent samples from different depths of one or more planet-like bodies.

The analogy between the Earth and meteorites is purely qualitative. No data have ever been presented to indicate that the weight ratio of the total of the stony meteorites and irons is identical with, or even similar to, the true average ratio of the silicate and metal phases within the Earth. Available information suggests that individual planets may differ considerably in bulk composition. Although it is not permissible to draw any conclusions as to the relative abundance of the silicate and metal phases in the Earth's interior on the basis of meteorite compositions, it seems reasonable to assume that roughly similar phases in the Earth's interior are arranged in concentric shells. According to current opinion, the Earth is composed of a

number of concentric shells or geospheres of varying chemical composition.

A concentric structure of the Earth is in accord with known geophysical data. Estimates of density and its variation with depth, velocity of earthquake waves, rigidity, etc., indicate the physical inhomogeneity of the Earth. A detailed discussion of these properties belongs to the field of geophysics and is, accordingly, outside the scope of this book. However, the consequences of the geophysical data are of importance to geochemistry. It may be assumed with a considerable degree of probability that the Earth is composed of the same phases as the meteorites are. It must, however, be ascertained that the suggested proportions of these phases and their arrangement in the Earth's interior give to the whole globe and to its different depths properties which are conformable with the geophysical data. In spite of many remarkable results and much provocative argument, it is apparent that geochemical hypotheses dealing with the chemical composition of the Earth's interior can hardly be more than guesses and approximations, the probability of which can be increased by further work, although absolute assurance is beyond reach.

Many hypotheses of the chemical composition and structure of the Earth's interior have been presented, but a detailed review of the arguments and deductions put forward by different authors is not within the scope of this book. In the following discussion, only the three principal hypotheses will be described, viz., those presented by H. S. Washington, V. M. Goldschmidt, and W. Kuhn and A. Rittmann.

HYPOTHESIS OF WASHINGTON

A schematic section of the Earth according to the hypothesis presented by Washington (1925) is given in Figure 3.1. The following shells are distinguished:

The central core is composed of metallic nickel-iron, corresponding to the metal phase of the meteoritic irons. It probably contains up to 5 per cent phosphides, carbides, sulfides, and carbon.

In its upper part the metallic core gradually passes over to the lithosporic shell that contains sporadically scattered segregations of ferromagnesian orthosilicate. The number of the silicate segregations increases with decreasing depth. The composition corresponds to that of the pallasites, with the average ratio of metal:silicate = 1:1. The iron:magnesium ratio in the silicate phase is approximately 1:5.

The overlying ferrosporic shell corresponds to the chondritic stony

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meteorites. The metal phase is present only in minor amounts and decreases in quantity with decreasing depth. In addition to the orthosilicate, this shell also contains ferromagnesian metasilicate and small amounts of calcium-aluminum silicate.

In the peridotitic shell the metal phase has disappeared. The composition corresponds to that of the achondritic stony meteorites. It contains more ferromagnesian metasilicate and calcium-aluminum silicate than does the underlying ferrosporic shell.

The basaltic shell has the composition of average plateau basalt, and the uppermost, mainly granitic, shell corresponds to the average igneous rock.

HYPOTHESIS OF GOLDSCHMIDT

Like Washington, Goldschmidt (1922, 1933b) also compared the Earth with meteorites. He pointed out that in a planet of sufficiently small size the weak gravitational field would not overcome friction at the boundaries between the different phases. Therefore, the molten metal, sulfide, and silicate phases cannot be completely separated from one another; consequently, no distinct shells are formed. The pallasites were assumed to represent pieces from small planet-like bodies in which segregation is not complete enough to permit formation of continuous shells. Owing to the stronger gravitational field, the separation within the Earth is, however, more complete.

Goldschmidt's hypothesis of the internal constitution of the Earth is schematically represented in Figure 3.2.

The innermost nickel-iron core, called the siderosphere, corresponds to the iron meteorites and contains 90 per cent iron, 8 per cent nickel, and 2 per cent other metals.

Goldschmidt, deviating from Washington, then compared the Earth with the products of an ore-smelting furnace. He assumed that the intermediate layer of the Earth between the iron core and the silicate crust is largely composed of oxides and sulfides of iron. This shell, called the chalcosphere, corresponds to the troilite phase of meteorites but contains considerable amounts of oxides.

The outermost shell, the lithosphere, is composed of silicates. Its inner part has a gabbroic bulk composition. It is surrounded by a more acidic outer shell, having a composition similar to that of the average igneous rock.

DISCUSSION

The numerical values originally given by Washington and by Goldschmidt for the thickness of the various shells, for their density,

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etc., do not agree in details either with one another or with the present information about the physical properties of the Earth's interior. Variation of the velocities of earthquake waves with depth indicates the presence of a number of discontinuities at definite depths, which represent sudden changes in physical properties. It is not known whether a change in physical properties at a certain depth is caused by a change in state of aggregation or by an actual change in chemical composition. The seismic discontinuities are of two kinds (Macelwane, 1939). A first-order discontinuity is a relatively sudden transition of the velocities, with a complete break in the depth-velocity curve. A second-order discontinuity is indicated by a change in the rate of the velocity increase or decrease, producing a more or less pronounced change in the slope of the depth-velocity curve.

Two main seismic discontinuities may be distinguished in the Earth's interior (cf. Jeffreys, 1929; Gutenberg, 1939):

1. The Mohorovičić discontinuity represents the uppermost major discontinuity and is found fairly uniformly under all continental regions at a depth varying from 30 to 50 km.

2. The Wiechert-Gutenberg discontinuity, at a depth of around 2,900 km, is the most striking of all discontinuities in the Earth's interior.

Between these two depths no first-order discontinuities have been found.

The existence of the two main discontinuities mentioned above forms the background for the generally accepted idea, according to which the Earth may be divided into three main spheres:

1. The *core* extending from the center of the globe to the Wiechert-Gutenberg discontinuity.

2. The *mantle* between the two discontinuities.

3. The *crust* from the Mohorovičić discontinuity to the surface. Within these main shells a number of second-order discontinuities occur. Up to the present time, only partial agreement has been reached by seismologists as to the number and respective depths of these discontinuities.

THE CORE

The center core of the Earth, called the siderosphere by Goldschmidt, is commonly believed to consist of metallic nickel-iron corresponding to the pure iron meteorites. Within the core one additional discontinuity has been discovered at a depth of 5,100 km (Jeffreys,

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1939*a*; Gutenberg and Richter, 1939), subdividing the core into an inner and an outer part. The existence of this discontinuity has been explained by assuming a content of occluded gas in the outer core (Daly, 1943). The inner core would then be less gas-charged.

THE MANTLE

The main difference between the hypotheses of Washington and Goldschmidt concerns the chemical composition of the mantle.

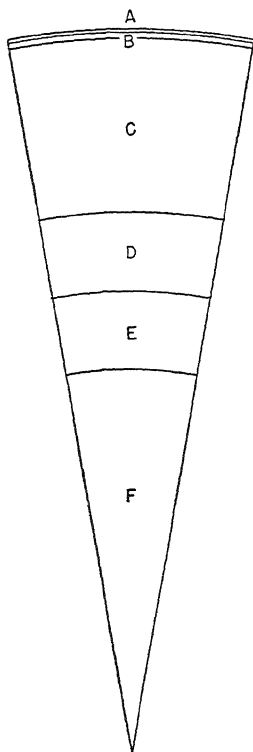


FIG. 3.1.—Washington's hypothesis of the internal constitution of the Earth

Zone	Depth of Region Occupied (km)	Thickness (km)
A. Granitic shell.....	0— 20	20
B. Basaltic shell.....	20— 60	40
C. Peridotitic shell.....	60—1,600	1,540
D. Ferrosporic shell.....	1,600—2,300	700
E. Lithosporic shell.....	2,300—3,000	700
F. Central core.....	3,000—6,400	3,400
Total.....		6,400

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Washington assumes a mixture of metal and silicate to be the essential material of the mantle, whereas Goldschmidt regards its deeper part as being a mixture of oxides and sulfides, mostly of iron (chalcosphere). Goldschmidt's main argument for his chalcosphere lies in the comparison of the Earth with an ore-smelting furnace. Provided that sulfur in the Earth's interior is sufficiently abundant to form a separate sulfide-oxide shell of the dimensions suggested by Goldschmidt, the analogy of the Earth with an ore-smelting furnace seems

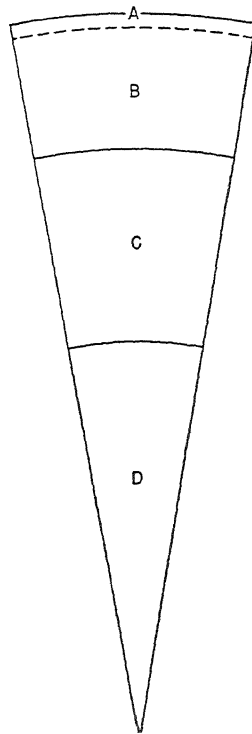


FIG. 3.2.—Goldschmidt's hypothesis of the structure of the Earth's interior

Zone	Density	Depth of Region Occupied (km)	Thickness (km)
A. Silicate crust.	2.8	0—120	120
B. Eclogite shell (compressed silicates)	3.6—4	120—1,200	1,080
C. Sulfide-oxide shell.	5—6	1,200—2,900	1,700
D. Nickel-iron core.	8—10	2,900—6,400	3,500
Total.			6,400

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very useful. Chemical analyses of meteorites do not indicate such a great abundance of sulfur, but close similarity of the Earth and meteorites is by no means necessary (Schwinner, 1936). More important for the present discussion is the fact that, according to metallurgical experience, the silicate slag of an ore-smelting furnace, overlying a sulfide layer, is always relatively richer in sulfur than is the silicate crust of the Earth (Linck, 1924; Niggli, 1928). If, therefore, a sulfide-oxide layer of a composition suggested by Goldschmidt underlies the Earth's silicate crust, the average abundance of sulfur in igneous rocks should be considerably greater than the statistical estimate, 0.052 per cent S, made by Clarke (1924).

Most geophysicists and geologists agree in principle with the supposed silicate composition of the mantle. It is very probable that the deeper parts of the Earth's interior, where silicate and metal are in contact with each other, carry most of the Earth's sulfur supply. The assumption that ferrous sulfide plays a major role in the mantle (up to 70 per cent, according to Tammann, 1923) is not generally accepted.

When the idea of a silicate mantle is accepted, two general trends in its composition seem to be natural, although not proved. First, in analogy with the chondrites, the mantle most probably is not entirely free of the metal phase but contains interstitial nickel-iron. The amount of the metal decreases with decreasing depth. Second, the main silicate phase also changes in composition with depth, becoming poorer in light elements at greater depths. With reference to these two trends and taking into account the available geophysical information, the following model of the structure of the mantle is presented, simplified from Daly (1943, 1946).

From the Wiechert-Gutenberg discontinuity at the depth of 2,900 km to the second-order discontinuity at the depth of about 950 km, the mantle is composed of a silicate material corresponding to the chondritic stony meteorites with interstitial nickel-iron. The metal-phase content decreases more or less gradually with decreasing depth.

From the 950-km level to the discontinuity at a depth of between 413 and 480 km, the material corresponds to the meteoritic achondrites without any metal phase.

The material between the top of the previous layer and the crust is peridotitic meteorite silicate (achondrite) and passes upward into gabbroic (basaltic) in composition. Above the depth of around 70 km it is crystalline and below that level partly vitreous (asthenosphere).

THE CRUST

Two main areas in the surface of the Earth can be distinguished:

1. The Pacific Basin, including the area between the American continent and the so-called andesite line (Born, 1933). Following the coast of Japan, this line extends southward, east of the Marianas Islands, and follows the archipelago to the area east of the Fiji Islands, where it turns again to the south. The Arctic Basin is probably part of this area.

2. The remainder of the Earth's surface, including all the continents and the Atlantic Ocean and the Indian Ocean up to the andesite line just mentioned.

In their crustal structure these two areas, Pacific and continental, differ from each other. In the continental areas, seismic and other data indicate the existence of three principal layers called the continental layers:

- a) The intermediate layer, overlying the Mohorovičić discontinuity, is probably richer in light elements than is the top of the mantle. In chemical composition it is probably intermediate between basalt and granite. Its top is found at depths varying from 10 to 30 km.

- b) The granitic layer, above the intermediate layer, corresponds in composition to the average of the igneous rocks of the Earth's surface. The designation granitic is not strictly correct because the average composition of the igneous rocks is rather granodioritic than granitic.

- c) The sedimentary layer is composed of sediments and of sedimentary and metamorphic rocks. Its greatest depths have been found in geosynclinal basins, in which it may extend down to 15 km.

The thickness and composition of the layers of the continental areas of the Earth's crust are subject to appreciable horizontal variation. The continental layers under the Atlantic and Indian oceans are considerably thinner than on the continents, and the granitic shell is possibly absent.

In the Pacific Basin the continental layers are entirely absent, the gabbroic (basaltic) substratum being in almost direct contact with the hydrosphere.

Referring only to chemical composition, the following designations are frequently used.

Sial (derived from *silicon-aluminum*): sedimentary and granitic layers with silicon and aluminum as predominant cations.

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Sialma (*silicon-aluminum-magnesium*): intermediate between Sial and Sima.

Sima (*silicon-magnesium*): from the deepest parts of the crust downward to where magnesium plays a more important role than aluminum.

The terms lithosphere and asthenosphere refer to the strength of the corresponding layers and have no connection with chemical composition. Accordingly, lithosphere is not an equivalent to the crust of the Earth as defined above. In the subsequent pages, however, the word lithogeochemistry usually refers to the geochemistry of the upper lithosphere. The reason for this incorrect use of the term lithogeochemistry is simply the fact that the uppermost lithosphere is the only part of the solid Earth on which direct geochemical observations can be made.

In addition to the shells or geospheres mentioned above, three outermost geochemical spheres are distinguished:

- a) The hydrosphere, which consists of the salt and fresh waters and the continental ice
- b) The atmosphere, the gaseous outer envelope of the Earth
- c) The biosphere, which comprises the living matter of the Earth

The structure and geochemistry of these three spheres will be discussed in forthcoming chapters.

HYPOTHESIS OF KUHN AND RITTMANN

All the hypotheses and views concerning the internal constitution of the Earth which are briefly summarized above are based on two fundamental concepts.

1. Seismic and other geophysical data show that the Earth may be subdivided into three main geospheres—the core, the mantle, and the crust.

2. The discontinuity at the outer boundary of the core indicates a sudden change in chemical composition. The core is supposed to consist of metallic nickel-iron.

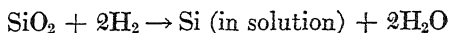
A hypothesis has been presented by Kuhn and Rittmann (1941) which abandons these two concepts. These authors pointed out that, according to present data, the Earth is supposed to be considerably richer in iron and poorer in magnesium, silicon, and oxygen than the Sun is. In addition, a very pronounced difference in the content of hydrogen and helium between the Earth and the Sun is suggested. On the assumption that the Earth is derived from the Sun, these dif-

ferences are hard to understand. On the other hand, taking into account the conditions supposed to prevail in the Earth's interior, the complete differentiation into an iron core and a silicate mantle is difficult to explain.

In order to avoid these difficulties, Kuhn and Rittmann assumed that the Earth's core does not consist of metallic nickel-iron but is composed of undifferentiated solar material. This material contains at least 30 per cent hydrogen. Originally, the whole Earth was a hot gaseous globe that was rapidly cooling through heat radiation and escape of hydrogen and helium from its gravitational field. The outer parts became poorer in these light gases and sank down. New light material was carried up, where it again lost its lightest material and sank down. In this way strong convection currents were produced that brought light material up to the surface and pushed heavier material down. However, this turbulence did not reach the center part of the globe, which remained unchanged in composition.

As a result of this process the internal constitution of the Earth is as follows: The center part of the Earth, up to about two-thirds of the radius from the center, is composed of original solar material. Overlying the center part there is a layer very rich in iron and other heavy elements. This layer represents the greatest depths that were affected by the convection currents and where, accordingly, the heavy elements were deposited. The outermost part of the globe is composed of the lighter elements, which form the present crust.

According to Kuhn and Rittmann, seismic discontinuities are not indications of changes in chemical composition at the corresponding levels. In their opinion, even the very striking first-order discontinuity at a depth of 2,900 km is caused merely by a sudden change in physical properties. The reason for this sudden change was explained by Kuhn (1948) in the following way: The free energy of the reaction



is positive at low temperatures. However, at high temperatures, such as those in the Earth's interior, it becomes negative, indicating that the reduction of silica by hydrogen is possible. The disappearance of silica or silicates in this way causes the sudden decrease of viscosity inferred from the seismic discontinuity at a depth of 2,900 km (Wiechert-Gutenberg discontinuity).

The hypothesis of Kuhn and Rittmann has so far attracted comparatively little attention. It merits, and will no doubt receive, both close study and extensive criticism in the immediate future.

DISTRIBUTION OF THE ELEMENTS AMONG THE GEOCHEMICAL SPHERES OF THE EARTH

GEOCHEMICAL AFFINITY

THE assumption that the supposed geochemical spheres of the Earth differ from one another in bulk chemical composition immediately brings up the problem of the distribution of the elements of the Periodic System among these spheres. If separate shells of different bulk composition exist in the Earth, the elements will be distributed among those shells in fixed proportions. This distribution obviously depends on the general chemical behavior of the element in question, on the physicochemical conditions present in the Earth's interior, and on the origin of the geospheres. The geochemical division of the Earth into a metallic core, a mantle consisting mainly of silicates, and a silicate crust only implies a hypothesis of the distribution of some few major elements that characterize the geospheres in question and are considered responsible for their main chemical features. The properties of these elements form the background for the distribution of all other elements.

Based on information concerning the abundance of the elements in the Universe, three base elements may be distinguished. Iron is the most abundant of all electropositive elements of the Earth, whereas oxygen and sulfur are the most important of the electronegative elements. These three elements and their mutual affinity relationships are largely responsible for the distribution during the first geochemical differentiation of the Earth.

The process of the formation of the geospheres in the Earth is comparable, to some extent, with the separation of the metal, sulfide, and silicate phases in an ore-smelting furnace. A study of the distribution of the elements in the metallurgical products and among the corresponding phases in meteorites, along with the information available of the manner of occurrence of the elements in minerals and

rocks in the upper lithosphere, reveals the general geochemical affinities of the elements. The geochemical affinity (Goldschmidt, 1937a) of an element is understood as the sum of its properties, which are responsible for its observed or supposed distribution. The affinity of an element for oxygen (or silica) and for sulfur, as compared with the corresponding affinity of iron, will determine the distribution of the element among metallic iron, iron sulfide, and iron silicate (oxide).

DISTRIBUTION OF THE ELEMENTS AMONG METAL, SULFIDE, AND SILICATE PHASES

An illustrative example of the distribution of the chemical elements among the molten metal, sulfide, and silicate phases has been given by Cissarz and Moritz (1933). These authors investigated the products obtained during metallurgical treatment of copper ore (*Kupferschiefer*) of the Mansfeld district in Germany. Their analyses of pig iron, copper matte, slag, flue dust, and copper ore are presented in Table 4.1, which shows that the elements from oxygen to tungsten are preferably enriched in the slag; those from sulfur to silver in the copper matte; those from zinc to lead in flue dust; and, finally, those from carbon to bismuth in pig iron. The elements of the first group are typical of silicate rocks, whereas most of the elements of the other groups may be readily precipitated as sulfides or reduced to the native state in the course of chemical analysis.

The application of the results obtained by Cissarz and Moritz to the present geochemical purpose is hindered by the circumstance that, in the Mansfeld ore, copper plays a quantitatively more important role than it does in the Earth. The sulfides separated during the treatment of the Mansfeld ore consist mainly of cupric sulfide (CuS). However, the general trend of the distribution is evident.

The distribution of the elements among the corresponding phases in meteorites (nickel-iron, troilite, silicate) is known by a large number of chemical analyses. A review of the results is presented in Table 4.2. The data given in this table are taken mostly from Goldschmidt (1937b), who gives a complete list of the original references. In some instances averages of the values given by various authors have been computed. For Cb and Ta the values given by Rankama (1944, 1947a) were adopted. The elements O, Mg, Al, Ca, Na, K, Sr, Ba, Sc, Li, Rb, Be, Hf, and Cs are practically absent in troilite and nickel-iron. As is evident from Tables 4.1 and 4.2, the distribution of the elements in meteorites and in the metallurgical products of the Mansfeld ore is largely similar.

GOLDSCHMIDT'S GEOCHEMICAL CLASSIFICATION OF THE ELEMENTS

Based on his hypothesis of the geochemical structure of the Earth, briefly summarized in chapter 3, Goldschmidt (1937*a*) has presented a general geochemical classification of the elements.

In Goldschmidt's opinion the enrichment of the elements, observed in the different phases of ore-smelting furnaces and of meteorites,

TABLE 4.1
DISTRIBUTION OF THE ELEMENTS AMONG THE METALLURGICAL
PRODUCTS OF THE MANSFELD COPPER ORE

ELEMENT	ORE, AVERAGE COMPOSITION	PIG IRON	COPPER MATTE	SLAG	FLUE DUST
	Per Cent				
O.....	38.36	2.39	0.58	42.30	n.d.
Na.....	0.6	~0.1	0.1	0.64	n.d.
Mg.....	2.9	0	0.05	7.46	n.d.
Al.....	7.5	0.05	0	9.11	n.d.
Si.....	15.5	0.02	0.05	22.09	4.03
K.....	~3.3	n.d.	0.49	3.28	n.d.
Ca.....	10.0	0.003	~0.001	13.50	n.d.
Ti.....	0.01	0.002	0.002	0.03	0
Cr.....	0.005	0	0	0.004	0
W.....	0.005	0	0	0.003	0
S.....	2.6	3.27	26.02	0.50	~20
Mn.....	0.3	0	0.64	0.2	~0.001
Cu.....	2.9	6.44	46.2	0.234	~3
As.....	0.08	0	0.02	0	0
Ag.....	0.016	0.015	0.252	0	0.03
Zn.....	0.9	0.0008	1.68	0.37	~40
Cd.....	0.05	0	~0.001	0	0.02
Pb.....	0.5	0.002	0.22	0.02	~10
C.....	9.0	1.16	n.d.	n.d.	n.d.
P.....	0.09	1.84	0	0.03	~0.005
V.....	0.05	0.08	~0.01	0.02	0.007
Fe.....	2.5	73.58	22.92	3.0	5.3
Co.....	0.004	2.44	0.25	0.004	0
Ni.....	0.01	1.72	0.28	0.05	0.002
Ge.....	n.d.	~0.005	0	0	0
Mo.....	0.03	6.64	0	0.002	~0.0005
Pd.....	~0.0001	~0.001	0	0	0
Sn.....	0.001	0.008	0	0	0
Sb.....	0.03	~0.001	0	0	0
Ir.....	~0.0001	~0.001	0.0008	0	0
Pt.....	~0.0001	0.0008	0	0	0
Au.....	~0.0001	0.0008	0	0	0
Bi.....	~0.01	~0.01	0.008	0	0

DISTRIBUTION OF THE ELEMENTS

most probably also took place in the corresponding geochemical spheres of the Earth. He pointed out that metallurgical experience may, however, be compared only to a certain degree with the conditions supposed to have prevailed in the interior of the Earth during the separation of the different phases. This is largely due to the fact that the reducing agent of an ore-smelting furnace is usually carbon, in contrast to hydrogen or hydrogen compounds in the case of the

TABLE 4.2
DISTRIBUTION OF SOME ELEMENTS AMONG THE NICKEL-IRON,
TROILITE, AND SILICATE PHASES OF METEORITES

ELEMENT	NICKEL-IRON	TROILITE	SILICATE
	g/ton		
Si.....	150	0	212,000
Cr.....	300	1,200	3,900
Mn.....	300	460	2,050
Ti.....	100	0	1,800
Zr.....	8	0	95
V.....	6	?	50
W.....	8 1	trace	18
Th.....	0.1	0	2
Cb.....	0.20	0	0.50
U.....	0 1	0	0.4
Ta.....	<0.06	0	<0.38
P.....	1,800	3,000	700
Zn.....	115	1,530	76
As.....	360	1,020	20
Cu.....	200	500	1.55
Cd.....	8	30	1.6
Ag.....	5	19	0
Sb.....	2	7 8	0.1
Bi.....	0 5	2	0.02
Tl.....	?	0.3	0.15
Ga.....	8	8	3
In.....	0.5	0 5	0.24
Ni.....	84,900	1,000	3,300
Co.....	5,700	100	400
Ge.....	500	30	5
Sn.....	100	15	5
Pb.....	56	20	2
Mo.....	16.6	11	2 5
Pt.....	16	3	0
Ru.....	15	8	0
Pd.....	13	2	0
Os.....	10	9	0
Rh.....	4	1	0
Ir.....	3	1	0
Au.....	2	0.5	0
Re.....	0.0082	0.001	0.0008

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Earth. Taking into account all information available on the chemical behavior of elements and on their manner of occurrence in the lithosphere and in meteorites, Goldschmidt divided the elements into three main geochemical affinity groups, presented in Table 4.3. However, the table is modified with reference to more recent information on the geochemical behavior of the elements. If an element belongs preferably to one group and, simultaneously, shows a less pronounced behavior characteristic of another group, it is given in parentheses in the latter case.

TABLE 4.3
GEOCHEMICAL CLASSIFICATION OF THE ELEMENTS

Siderophile	Chalcophile	Lithophile	Atmophile	Biophile
Au	Cu Ag	Li Na K Rb Cs	H C N	H C N O P
Ge Sn (Pb)	Zn Cd Hg	Fa	O I Hg	(Na) (Mg) (S) (Cl)
C P (As)	Ga In Tl	Be Mg Ca Sr Ba	He Ne A	(K) (Ca) (Fe)
Mo (W)	(Ge) (Sn) Pb	Ra	Kr Xe Rn	(B) (F) (Si)
Re	As Sb Bi	(Zn) (Cd)		(Mn) (Cu) (I)
Fe Co Ni	(Mo)	B Al Sc Y		
Ru Rh Pd	S Se Te	La Ce Pr Nd Sm		
Os Ir Pt	Fe (Co) (Ni)	Eu Gd Tb Dy Ho		
	(Ru) (Pd) (Pt)	Er Tm Yb Lu Np		
		Ac Th Pa U		
		Pu Am Cm		
		Ga (In) (Tl)		
		C Si Ti Zr Hf		
		(Ge) (Sn) (Pb)		
		V Nb Ta		
		P (As)		
		O Cr W Mn		
		(Fe) (Co) (Ni)		
		H F Cl Br I		

In Goldschmidt's classification the siderophile elements are preferably enriched in the nickel-iron core (siderosphere). The elements of this group are characterized by a relatively weak affinity for oxygen and sulfur. They are, in addition, readily soluble in molten iron either as native elements or alloyed with iron.

The chalcophile elements show a strong affinity for sulfur. They are readily soluble in molten iron monosulfide and are enriched in the sulfide-oxide shell (chalcosphere).

The lithophile elements are enriched in the silicate crust (lithosphere). They show a strong affinity for oxygen.

Along with the three main groups given, the most typical elements of the atmosphere (atmophile elements) and of the biosphere (biophile elements) are included in Table 4.3.

The distribution of the electropositive elements among metal, sulfide, and silicate phases is controlled by the free energies of formation of the corresponding sulfides and silicates, as compared with

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those of ferrous sulfide and ferrous silicate, according to the following general reactions (Me means any cation except iron):

- (1) Fe silicate + Me \rightarrow Me silicate + Fe ;
- (2) Fe sulfide + Me \rightarrow Me sulfide + Fe ;
- (3) Fe silicate + Me sulfide \rightarrow Me silicate + Fe sulfide .

In the absence of adequate thermal data for silicates, Wahl (1910), Goldschmidt (1945), and Brown and Patterson (1948) have considered the oxides instead of silicates in reactions (1) and (3). Because

TABLE 4.4
FREE ENERGY OF FORMATION ($-\Delta F^\circ$) OF SOME OXIDES FROM STANDARD
STATES OF THE ELEMENTS IN KILOGRAM-CALORIES PER GRAM
ATOM OF OXYGEN AT ROOM TEMPERATURE

Oxide	Free Energy of Formation $-\Delta F^\circ$	Oxide	Free Energy of Formation $-\Delta F^\circ$
CaO.....	144 3	In ₂ O ₃	72 7
MgO.....	136 2	SnO.....	60 8
Al ₂ O ₃	125 6	FeO.....	59 3
ZrO ₂	122 7	WO ₃	59 1
V ₂ O ₃	103.7	CdO.....	55 2
TiO ₂	102 5	NiO.....	53 0
SiO ₂	95 2	MoO ₃	52 7
Na ₂ O.....	93.6	Sb ₂ O ₃	49 7
Ta ₂ O ₅	89.4	PbO.....	45 1
MnO.....	86 9	As ₂ O ₃	44 9
Cr ₂ O ₃	85 2	Bi ₂ O ₃	38 9
Cr ₂ O ₃	85 1	Cu ₂ O.....	35 1
Ga ₂ O ₃	78 3	Ag ₂ O.....	2 6
ZnO.....	75.8		

the heat of formation (ΔH°) of a compound from the standard states of the elements is usually the prime contributor to its free energy (ΔF°) of formation, a rough solution of the problem may be obtained on the basis of the heat-of-formation values for the oxides of the metals. In Table 4.4, however, the free energies of formation of the oxides of some electropositive elements are given, expressed in kilogram-calories per gram atom oxygen. The data underlying the figures in this table are taken mainly from Bichowsky and Rossini (1936), Latimer (1938), and Kelley (1941). In several instances the heats of formation and the entropies of the oxides are known only approximately, and, accordingly, the corresponding free-energy values are subject to considerable uncertainty.

As is seen from Table 4.4, the lithophile elements have higher free energy of formation of the oxide than does ferrous iron. On the other

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hand, the elements with lower free energy of formation of the oxides belong to the siderophile and chalcophile groups. Remarkable exceptions to this rule are gallium, zinc, and indium. This may be due to the fact that these elements, owing to their low abundance in igneous rocks, are not able to form separate gallium, zinc, or indium minerals but occur disseminated in the structures of other compounds. Accordingly, the distribution of these elements among metal and silicate is not controlled by the thermal properties of their pure compounds but by the energy balances connected with the corresponding isomorphous substitutions.

TABLE 4.5
FREE ENERGY OF FORMATION ($-\Delta F^\circ$) OF SOME SULFIDES FROM STANDARD STATES OF THE ELEMENTS
IN KILOGRAM-CALORIES PER GRAM ATOM OF SULFUR
AT ROOM TEMPERATURE

Sulfide	Free Energy of Formation $-\Delta F^\circ$
ZnS.....	40.4
CdS.....	33.5
MoS ₂	27.1
FeS.....	23.4
WS ₂	23.1
PbS.....	22.7
Tl ₂ S.....	22.5
NiS.....	21.3
CoS.....	21.1
Cu ₂ S.....	20.6
PtS.....	18.6
Bi ₂ S ₃	13.0
Sb ₂ S ₃	12.3
Ag ₂ S.....	8.7

As shown by Brown and Patterson (1948), a corresponding treatment of the sulfides reveals little or no relationship between free energy of formation of the solid sulfides and distribution of the sulfide-forming elements among troilite and nickel-iron in meteorites. This is true also for the sulfide and metal phases in the metallurgical products of the Mansfeld ore. The free energies of formation of the sulfides of some metals from the standard states are given in Table 4.5. The data of this table are selected from the review presented by Kelley (1937). It is evident that nickel and cobalt have slightly lower values and, for instance, zinc and cadmium have higher values for the free energy of formation than does ferrous iron. Accordingly, the observed distribution of these metals among metal and sulfide is in agreement with the free-energy

DISTRIBUTION OF THE ELEMENTS

data. On the other hand, despite their enrichment in the sulfide phase, copper and silver, for example, have lower free-energy values than does ferrous iron. A thorough thermodynamic treatment of the distribution of the electropositive elements among metal, sulfide, and silicate phases appears highly desirable.

As pointed out by Niggli (1928), a close relationship exists between the geochemical behavior of the elements and their position in the Periodic Chart. This relationship is illustrated in Table 4.6. The

TABLE 4.6*
PERIODIC SYSTEM AND THE GENERAL GEOCHEMICAL
CHARACTER OF THE ELEMENTS

H							He	
Li	Be	B	C	N	O	F	Ne	
Na	Mg	Al	Si	P	S	Cl	A	
K <i>Cu</i>	Ca <i>Zn</i>	Sc <i>Ga</i>	Ti Ge	V <i>As</i>	Cr <i>Se</i>	Mn Br	Kr	Fe Co Ni
Rb <i>Ag</i>	Sr <i>Cd</i>	Y <i>In</i>	Zr Sn	Cb <i>Sb</i>	Mo <i>Te</i>	Tc? I	Xe	Ru Rh Pd
Cs Au	Ba <i>Hg</i>	La-Lu <i>Tl</i>	Hf <i>Pb</i>	Ta <i>Bi</i>	W <i>Po?</i>	Re At?	Rn	Os Ir Pt
Fa	Ra	Ac-Cm						

* **Au**: siderophile; *Cu*: chalcophile; *Li*: lithophile (and atmophile).

geochemical character of the element depends largely on the electron configuration of its atom for the following reasons:

1. As emphasized by Goldschmidt in several papers (e.g., 1930a), the lithophile metals form ions of the noble-gas type having 8 electrons in the outermost shell. The volumes of the neutral atoms are relatively large. Illustrative examples are, among others, alkali and alkaline-earth metals. Vanadium, chromium, and manganese are exceptions to this rule. Despite their strongly lithophile character, their most stable and most abundant ions in Nature (Mn^{2+} , Cr^{3+} , V^{3+}) deviate from the noble-gas type.

2. The chalcophile metals have 18 electrons in the outermost shells in their ions. Their atomic volumes are small. They include copper, zinc, gallium, and others.

3. The outermost shells of the ions of the siderophile metals are mostly incompletely filled. The atomic volumes are remarkably

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small, generally occupying the minima in the atomic volume-atomic number curve. Iron, cobalt, nickel, and the precious metals, among other elements, belong to this group.

PROBABLE DISTRIBUTION OF THE ELEMENTS IN THE EARTH

As mentioned in chapter 3, the hypothesis put forward by Goldschmidt concerning the existence of a separate sulfide-oxide sphere (chalcosphere) in the Earth's interior is doubtful and not generally accepted. Therefore, the experience gained from metallurgical processes cannot be immediately extended to the Earth. The division of the elements into the three main geochemical affinity groups merely characterizes their distribution in the molten metal, sulfide, and silicate phases, regardless of the actual influence of this distribution upon the enrichment of the elements in the various geochemical shells of the Earth. The division indicated above is, however, very illustrative and useful for many geochemical purposes. In this book the terms siderophile, chalcophile, and lithophile are used in a purely chemical sense without reference to any supposed distribution among the geochemical shells.

Analogy with the meteorites makes it very probable that the mantle between the nickel-iron core and the silicate crust in the Earth, supposed to be composed mainly of chondritic silicate material, contains much of the Earth's sulfur supply. The average sulfide content of chondrites given as FeS (troilite), according to Table 1.4, is about 5 per cent. If this figure is applied to the chondritic mantle, it means that iron sulfide is merely a minor constituent thereof, as compared with its silicate portion. Of course, the iron sulfide was able to collect and concentrate the elements which are chalcophile under the conditions prevailing during the formation and separation of the sulfide material.

In general, the geochemical behavior of an element, as indicated by its distribution among the three phases, depends on the conditions under which these phases have been separated. Chromium affords a striking example of this fact. Under conditions prevailing in the lithosphere, chromium shows no noticeable affinity for sulfur. On the other hand, it is chalcophile in meteorites, in which it occurs in daubréelite (FeCr_3S_4). This difference in the geochemical behavior of chromium in the lithosphere and in the meteorites is apparently due to the difference in the degree of oxidation in the terrestrial rocks and in meteorites.

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As a matter of fact, relatively few elements are strongly chalcophile when occurring in meteorites. The most important among them are, according to Goldschmidt (1937*b*), sulfur, selenium, chromium, silver, and zinc. Some other elements, like gallium, indium, thallium, antimony, and bismuth, which are often enriched in sulfides and related compounds in the lithosphere, also show a remarkable siderophile trend in meteorites.

The above discussion shows that the geochemical character is by no means very sharply established for all elements, not even under strictly determined conditions. It sounds reasonable to assume that under given conditions the distribution of the elements in the metal, sulfide, and silicate phases corresponds to an equilibrium, which most probably varies with the conditions. It may be assumed that the typically siderophile elements, listed in Table 4.3, are enriched in the nickel-iron core of the Earth. The chalcophile elements most likely occur enriched in the accessory sulfide phase in the intermediate basic mantle but might be present to some extent also in the nickel-iron core. In addition, it must be kept in mind that, according to their metallurgical behavior, a number of the chalcophile metals are strongly enriched in the flue dusts of the ore-smelting furnaces (Zn, Cd, Pb, in Table 4.1), from which many of them (Ga, In, Tl, Hg, Ge, Sn, Pb, Sb, Bi, Se, Te, etc.) are obtained in commercial quantities as by-products. Consequently, it may be expected that these elements have been partially separated in this way from the sulfide phase or even from the metal phase during the first geochemical differentiation of the Earth. The compounds corresponding to the flue dusts are now present in the uppermost lithosphere, together with the true lithophile elements. Among the lithophile elements, those belonging to the late-magmatic stage of crystallization are enriched in the Earth's outermost crust. This enrichment is a result of the fractional crystallization of magmas and represents the second geochemical differentiation of the Earth.

GEOCHEMISTRY OF THE LITHOSPHERE

GEOCHEMICAL CHARACTERIZATION OF THE ELEMENTS IN THE LITHOSPHERE

THE division of the elements into three groups according to their geochemical behavior, introduced by V. M. Goldschmidt and presented in chapter 4, is based on their observed or supposed distribution among the metal, sulfide, and silicate phases. Consequently, the corresponding group names (siderophile, chalcophile, and lithophile elements) refer to a three-phase system and indicate a more or less pronounced tendency of an element to become enriched in one of these phases as compared with the other two. In contrast to the whole Earth (or all meteorites and metallurgical products), the upper lithosphere represents but a two-phase system, in which free metal is virtually absent. Therefore, the classification for a three-phase system with the corresponding designations mentioned above cannot be strictly applied to the geochemical characterization of the elements in the lithosphere.

A geochemical classification of the elements suitable for the conditions prevailing in the lithosphere was suggested by Washington (1920). He established the presence of two groups:

1. The petrogenic elements which occur in Nature primarily as oxides, silicates, fluorides, and chlorides.
2. The metallogenic elements which normally form sulfides, selenides, tellurides, arsenides, antimonides, bromides, and iodides or occur as native elements.

This classification is based on the manner in which elements occur in minerals. A certain element is included in the petrogenic or in the metallogenic group according to its observed concentration in one of the series of compounds listed above. In other words, the average percentage of the element in the two groups of compounds is used as the basis of classification.

Washington's original classification must now be considered obsolete for a number of elements. Therefore, it is not reproduced in detail in this connection. However, a classification made according to his principle is illustrative with reference to the general geochemical behavior of the elements because it indicates the general trend of their distribution among sulfide and silicate, etc. For geochemical purposes it is still more important to consider in the lithosphere the ratio between the amount of an element contained in compounds formed with oxygen (fluorine, chlorine) and the amount present in sulfides and related compounds or in the native state. The independent minerals of an element, of course, illustrate rather well its general geochemistry. On the other hand, in the case of trace elements, which usually occur in minerals in subordinate amounts as substitutes for certain carrier elements, such a manner of occurrence is often geochemically more characteristic. For example, thallium is a typically metallogenic element which sometimes occurs in sulfide deposits in remarkably high amounts and is obtained in commercial quantities from the flue dusts of such ores. In fact, the only independent thallium minerals are sulfides—crookesite, $\text{Cu}_{15}\text{Tl}_2\text{AgSe}_9$; lorandite, $\text{Tl}_2\text{S} \cdot \text{As}_2\text{S}_3$; hutchinsonite, $\text{PbS} \cdot (\text{Ag}, \text{Tl})_2\text{S} \cdot 2\text{As}_2\text{S}_3$; and vrbaite, $\text{Tl}_2\text{S} \cdot 2\text{As}_2\text{S}_3 \cdot \text{Sb}_2\text{S}_3$. These species are, however, only mineralogical curiosities. Geochemically, the most important manner of occurrence of thallium is its camouflage in minerals containing rubidium (see chap. 40). The $\text{Rb}:\text{Tl}$ ratio in feldspars, micas, etc., is fairly constant (Ahrens, 1945). Certainly, the most part of the thallium found in the lithosphere is contained in these silicate minerals.

For the reason mentioned above, the principle of classifying the elements followed by Washington will not be applied in this book. A new grouping is introduced for the geochemical classification of the elements in the lithosphere, based on their quantitatively most important manner of occurrence therein, as follows:

1. The elements occurring exclusively, or at least for the most part, combined with oxygen in oxides, silicates, phosphates, carbonates, nitrates, borates, sulfates, etc., are called oxyphile. Oxygen may be replaced by fluorine or chlorine to a minor extent. Ionic bonds usually prevail in the crystal structures of these minerals.

2. The available supply of certain other elements in the lithosphere occurs preferentially in minerals free of oxygen (fluorine, chlorine), i.e., mostly as sulfides, selenides, tellurides, arsenides, antimonides, intermetallic compounds, native elements, etc. These elements are

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called sulfophile. The bonds in the structures of these minerals are covalent or metallic.

Like the classification of Goldschmidt for a three-phase system and that of Washington for a two-phase system, the classification adopted here is also by no means unequivocal; all intermediate steps between the two groups are represented among the elements. Because the principle of this grouping differs from the previous classifications, new names are used for the groups distinguished.

The most typically oxyphile elements are, with few exceptions, those which were called lithophile by Goldschmidt and petrogenic by Washington. They are shown in the accompanying tabulation. These elements occur in the lithosphere nearly always combined with oxygen (fluorine, chlorine). Manganese and, to a very small extent, vanadium are found in some sulfides. For the present purpose, this manner of occurrence of manganese and vanadium is rather unimportant geochemically.

H	Li	Be	B	C	N	O	F
	Na	Mg	Al	Si	P		Cl
	K	Ca	Sc	Ti	V	Cr	Mn
	Rb	Sr	Y	Zr	Cb		
	Cs	Ba	La-Lu	Hf	Ta	W	
		Ra	Ac-U				

According to the adopted terminology, the elements called siderophile and chalcophile by Goldschmidt and metallogenic by Washington represent, again with some exceptions, a continuous series from the oxyphile to the sulfophile group. In order to elucidate the geochemical behavior of these elements under the conditions prevailing in the lithosphere, the following remarks are presented.

The average sulfur content of igneous rocks is, according to Table 2.3, 0.052 per cent S (Clarke, 1924). This corresponds to about 0.14 per cent sulfides, given as FeS. These figures give the average amount of sulfur contained in ordinary igneous rocks without any detectable late magmatic or metasomatic addition of sulfides. Sulfur is largely concentrated in late magmatic solutions (see chap. 43). On the other hand, it shows a pronounced tendency to become mobilized in regional metamorphism. The solutions formed, either primary magmatic or secondary metasomatic, give rise to sulfide deposits or enter secondarily the ordinary igneous rocks, causing an abnormally high sulfur content therein. Although these sulfide deposits are of great economic importance, they apparently are geochemically negligible.

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It would be important to estimate the mass of the sulfide bodies in the upper lithosphere and to determine the distribution of sulfur between the accessory sulfide phase of ordinary igneous rocks and the separated sulfide bodies. So far, a reasonable basis for such calculations is unknown. Obviously, the greatest part of the sulfide deposits is of no economic value. The fact, however, that the mass of the sulfide deposits evidently is extremely small as compared with the mass of the whole lithosphere seems to justify their omission when calculating the average composition of the sulfide phase of the igneous rocks.

TABLE 5.1
APPROXIMATE COMPOSITION OF THE MOST ABUNDANT ACCESSORY
SULFIDES OF THE IGNEOUS ROCKS

ELEMENT	PYRITE	PYRRHOTITE	CHALCOPYRITE	PENTLANDITE
	Per Cent			
Fe.....	47	61	31	31
Cu.....			34	
Ni.....				35
Co				1
S.....	53	39	35	33
Total	100	100	100	100

Microscopic investigation reveals that pyrite, pyrrhotite, chalcopyrite, and pentlandite are the most abundant among the accessory sulfide constituents of common igneous rocks (Newhouse, 1936; Ramdohr, 1940). Their approximate chemical composition is given in Table 5.1.

On the basis of the values recorded in this table, the average sulfur content of the igneous sulfide phase is calculated as 40 per cent S. This means that sulfur has become enriched in the sulfide phase by $40/0.052$, or about 750 times. If the elements forming sulfides in the lithosphere were enriched in the accessory sulfide phase of igneous rocks by the same factor as sulfur is, the sulfide phase would have the composition given in Table 5.2, second column. For comparison, the average composition of 57 primary magmatic sulfides given by Noddack and Noddack (1931a) is presented in Table 5.2. The composite sample analyzed consisted of 35 pyrrhotites, 10 primary pyrites, 8 pentlandites, and 4 nickelian pyrites from different localities and was

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considered to represent magmatic sulfides in general. No data were given concerning the geological background of the samples.

Comparing the first and second columns of Table 5.2 and taking into account the information available on the composition of accessory sulfides of igneous rocks, one may reach the following conclusions concerning the oxyphile or sulfophile character of the elements in question.

TABLE 5.2
ABUNDANCE OF SOME ELEMENTS IN IGNEOUS ROCKS
AND IN MAGMATIC SULFIDES

Element	Abundance in Igneous Rocks (Per Cent)	Abundance Mul- tplied by 750 (Per Cent)	Average Com- position of 57 Magmatic Sulfides (Per Cent)
Cu.....	0.007	5.25	1.09
Ag.....	0.00001	0.0075	0.001
Zn.....	0.0132	9.90	0.85
Cd.....	0.000015	0.011	0.002
Ga.....	0.0015	1.13	0.0002
In.....	0.00001	0.0075	0.00004
Tl.....	0.00003-0.0003	0.023-0.23	0.00001
Ge.....	0.0007	0.53	0.001
Sn.....	0.004	3.0	0.005
Pb.....	0.0015	1.13	0.001
As.....	0.0005	0.38	0.006
Sb.....	0.0001	0.075	0.0001
Bi.....	0.00002	0.015	0.0002
Mo.....	0.00025-0.0015	0.19-1.13	0.002
S.....	0.052	40	40.4
Se.....	0.000009	0.0068	0.02
Te.....	0.00000018	0.00014	0.0002
Co.....	0.0023	1.73	0.21
Ni.....	0.008	6.0	3.14

Copper.—If all copper is contained in chalcopyrite (and in other less abundant copper sulfide minerals), the values for Cu in the third and fourth columns of Table 5.2 should be equal. The value in the second column is derived from the average copper content of igneous rocks given by Sandell and Goldich (1943). Their value is largely based on analyses of American igneous rocks of Minnesota and Michigan which might deviate from the world's average. On the other hand, in the composite sample analyzed by Noddack and Noddack no chalcopyrites were included, and consequently it might not exactly represent the true average of accessory magmatic sulfides as far as copper is concerned. The fact that the two figures are roughly of the same order of magnitude makes it very probable that at least a great

part of copper is combined with sulfur. As emphasized by Ramdohr (1940), there appears to be evidence indicating that chalcopyrite, on an average, is abundant enough to be responsible for most of the copper present in rocks. However, it is highly probable that in some instances copper enters the structures of the rock-forming silicates. Consequently, copper seems to be sulfophile, but this character is not very pronounced.

Silver.—The figures given in Table 5.2 seem to indicate that silver, like copper, is mostly contained in sulfides. According to Joensuu (1948), 79 accessory chalcopyrites from different igneous and metamorphic rocks of the pre-Cambrian formations in Finland contain about 0.02 per cent Ag, on an average. On the other hand, silver is not known to occur in the structures of rock-making silicates. The sulfophile character of silver is apparently stronger than that of copper.

Gold.—Owing to the low abundance of gold in the upper lithosphere, data concerning its occurrence in accessory sulfides and in silicates of ordinary igneous rocks are very scanty. The remarkable tendency of gold to occur as native element makes its strong sulfophile character highly probable.

Zinc.—In view of the relatively great abundance of zinc in the upper lithosphere, it is surprising that sphalerite is exceedingly scarce among the accessory sulfides of ordinary igneous rocks (Newhouse, 1936; Ramdohr, 1940). So far, it is unknown to what extent zinc is able to enter the structures of pyrite, pyrrhotite, and chalcopyrite under conditions prevailing during the formation of these minerals in Nature. The observed scarcity of sphalerite in rocks agrees very well with the figures for zinc given in Table 5.2. Zinc is most probably an oxyphile element. Its oxyphile character is apparently less pronounced than that of gallium and germanium (see below).

Cadmium.—With reference to its general geochemical character in the lithosphere, cadmium is very similar to zinc and must be included in the oxyphile group. However, the oxyphile character of cadmium is, perhaps, slightly weaker than that of zinc. According to Sandell and Goldich (1943), the average Zn: Cd ratio of igneous rocks is approximately 530:1. On the other hand, the average cadmium content of 78 Swedish sphalerites given by Gabrielson (1945) is 0.173 per cent Cd. The corresponding Zn: Cd ratio is about 320:1. A still higher cadmium content is obtained from 79 Norwegian sphalerites analyzed by Oftedal (1940), viz., 0.25 per cent Cd. From this mean the

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most Cd-rich sphalerites (>1 per cent Cd) reported by Oftedal have been left out as exceptional cases. Accordingly, cadmium appears to have a slight tendency to become enriched in sphalerite in respect to zinc.

Mercury.—Data for the mercury content of accessory sulfides and of rock-making silicates are too scarce to allow any reliable conclusions regarding its oxyphile or sulfophile character. However, mercury might be sulfophile because of its marked tendency to occur in the native state.

Gallium.—Although the gallium content given by Noddack and Noddack for magmatic sulfides (Table 5.2) may be too low, the very strongly oxyphile character of this metal is evident.

Indium.—In addition to the average indium content of magmatic sulfides given by Noddack and Noddack (Table 5.2), the averages shown in the accompanying tabulation for sulfide minerals of geo-

Material Analyzed	In (Per Cent by Weight)
Average of 10 pyrites from Finland (Erämetsä, 1938) . . .	<0.0001
Average of 10 pyrrhotites from Finland (Erämetsä, 1938)	<0.0001
Average of 21 chalcopyrites from Finland (Erämetsä, 1938)	0.001
Average of 21 sphalerites from Finland (Erämetsä, 1938) . .	0.005
Average of 78 sphalerites from Sweden (Gabrielson, 1945)	0.0047

logically different origin are reported in literature. According to the analyses given by Oftedal (1940), the Norwegian sphalerites contain, on an average, nearly as much indium as do the Finnish and Swedish sphalerites mentioned above. These figures clearly indicate that only a small part of the indium supply in the lithosphere is contained in sulfides. Consequently, indium belongs to the oxyphile group, but its oxyphile character is certainly weaker than that of gallium.

Thallium.—No data on the thallium content of accessory pyrites and pyrrhotites are available. According to Joensuu (1948), the average for 79 Finnish chalcopyrites is 0.001 per cent Tl. The close relationship between thallium and rubidium in potassium minerals (Ahrens, 1945) evidently justifies the inclusion of thallium in the oxyphile group.

Germanium, tin, lead.—Like gallium, these three elements are evidently very strongly oxyphile.

Arsenic, antimony, bismuth.—The present abundance data, especially in the case of antimony and bismuth, are not very reliable. It appears, however, that all these elements are oxyphile (for arsenic see Ramdohr, 1940).

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Molybdenum.—Although frequently found in some granites and granite pegmatites, molybdenite apparently is rather scarce in igneous rocks (Ramdohr, 1940). This fact and the figures of Table 5.2 indicate that molybdenum is oxyphile. Further investigations concerning its occurrence in rock-making silicates and other oxygen-containing minerals are highly desirable.

Sulfur, selenium, tellurium.—As may be expected, these three elements, according to Table 5.2, are sulfophile. The occurrence of sulfates, selenates, and tellurates is obviously of minor geochemical importance.

Cobalt, nickel.—The values for cobalt and nickel given in Table 5.2 indicate that these metals mostly enter the structures of the oxygen-containing minerals. The values obtained by Noddack and Noddack

TABLE 5.3
AVERAGE COBALT AND NICKEL CONTENT OF ACCESSORY
PYRITES, PYRRHOTITES, AND CHALCOPYRITES FROM
FINNISH PRE-CAMBRIAN ROCKS

Mineral	Number of Analyses	Co (Per Cent)	Ni (Per Cent)
Pyrite	172	0.2	0.09
Pyrrhotite	92	0.07	0.2
Chalcopyrite	79	0.01	0.04

depend largely on the number of pentlandites and nickelian pyrites included in the composite sample analyzed. Therefore, the question may be raised whether the mixture analyzed by Noddack and Noddack really represents the average composition of primary magmatic sulfides in respect to cobalt and nickel. On the other hand, according to Newhouse (1936) and Ramdohr (1940), pentlandite is decidedly less abundant as an accessory constituent of ordinary igneous rocks than is chalcopyrite. This fact and the average cobalt and nickel content of accessory pyrites, pyrrhotites, and chalcopyrites indicate that these metals must be oxyphile (see Ramdohr, 1940). The average cobalt and nickel content of the Finnish pre-Cambrian pyrites, pyrrhotites, and chalcopyrites, analyzed by Joensuu (1948), is given in Table 5.3.

Ruthenium, rhodium, palladium, osmium, iridium, platinum.—As for gold, data for the content of the platinum metals in accessory igneous sulfides and in the rock-making silicate minerals are scanty. It appears very likely that these metals belong to the sulfophile group.

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The general trend in the variation of the oxyphile and sulfophile character of elements in a part of the Periodic System is illustrated in Table 5.4. For the elements listed in this table, the sulfophile character evidently becomes stronger (the oxyphile character weaker) when passing from the right to the left. In a vertical column the sulfophile character usually increases when passing downward. An exception to this rule is thallium, which appears to be more strongly oxyphile than does indium. This might be due to the change of valence because thallium is mostly univalent in minerals, instead of being trivalent as required by its position in the Periodic System.

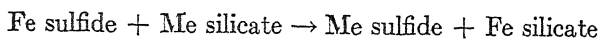
The discussion presented above shows that the distribution of elements between silicates (fluorides, chlorides) and sulfides (selenides,

TABLE 5.4
VARIATION OF THE OXYPHILE AND SULFOPHILE CHARACTER
OF ELEMENTS IN PART OF THE PERIODIC SYSTEM

Cu*	Zn	Ga	Ge
Ag	Cd	In	Sn
Au	Hg?	Tl	Pb

* Cu : sulfophile; Zn: weakly oxyphile; Ge strongly oxyphile.

arsenides, etc.) in the lithosphere does not depend solely on their chemical affinity for oxygen (fluorine, chlorine) and for sulfur (selenium, arsenic, etc.), respectively. The chemical affinity is determined by the free energies of formation of the corresponding silicates and sulfides. Thermodynamically, the free energy of the general reaction

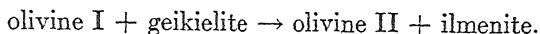


indicates which one of the two groups of compounds—sulfide or silicate—is preferred by the element (Me). This reaction shows the most stable distribution between the pure compounds, which are present in the system in equimolecular amounts. In the lithosphere, however, the sulfide phase is very scarce. When determining the thermodynamically most stable distribution of an element between the two groups of compounds, the isomorphic replacement phenomena must be taken into account. To the free energies of formation of the compounds in question must be added the free energies of formation of the possible isomorphic mixtures.

The influence of the free energy of isomorphic replacement on the

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stability of a mineral or of a mineral association was illustrated by Sahama and Torgeson (1949) by means of the following reaction:



The difference in the free energy of formation of olivine I and olivine II, due to a corresponding difference in entropy of mixing of Mg_2SiO_4 and Fe_2SiO_4 in the two olivines, affects the stability relationships of geikielite (MgTiO_3) and ilmenite (FeTiO_3) in such a way that the mixture geikielite + olivine is stable at high temperatures and the mixture ilmenite + olivine at low temperatures.

This example shows that the possibility of isomorphic substitution might, in some cases, result in a distribution of an element between the sulfide and silicate phases which deviates from that expected on the basis of the affinity relationships between the element and oxygen or sulfur.

Because of isomorphic substitution, a number of siderophile or chalcophile or metallogenic elements have a more or less pronounced oxyphile character in the lithosphere, indicating that the bulk of the elements present enters the structures containing oxygen (fluorine, chlorine). This fact shows the great importance of crystal chemical considerations in geochemistry. The isomorphic substitution depends on the crystal structures of rock-making minerals and on the properties of the ions and atoms of elements.

CRYSTAL CHEMISTRY AND GEOCHEMISTRY

SIGNIFICANCE OF CRYSTAL CHEMISTRY IN GEOCHEMISTRY

According to the definition of geochemistry adopted for this book, one of the principal aims of geochemical research is the detection of the laws which dominate the manner of occurrence of the elements in the Earth. When the content of an element in rocks, minerals, and other natural products has been established, a general outline of its geochemical behavior may be presented, which must be explained, that is, the reason for the manner of occurrence of the element must be found and must be based on physical and chemical laws. An explanation of the geochemical behavior of an element is often sought in the rather vague term, general chemical properties of the element. Chemically, the element is characterized by its ability to react with other elements and by the conditions in which the compounds formed are stable. The knowledge of the chemical properties does not

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always suffice to make the true manner of occurrence of an element thoroughly understood. Thus, e.g., the quantity of an element in a mineral does not explain the structural role of the element in the structure of the mineral in question. The structural positions of the atoms and ions of an element in minerals essentially affect the manner of occurrence of the element. The crystal structures of minerals and the properties of atoms and ions largely regulate the incorporation of elements in minerals and, consequently, strongly influence their geochemical behavior.

The great importance of crystal chemical considerations in litho-geochemistry may be illustrated by the following example. Lead and potassium show hardly any parallelism in chemical behavior. Therefore, no geochemical relationship or coherence can be expected in their manner of occurrence in the lithosphere if no attention is paid to crystal chemical properties. However, the bulk of the lead in the lithosphere evidently does not occur in sulfide minerals but rather in potassium minerals, such as potash feldspar and micas. To explain this fact it has been suggested that potassium is replaced by lead in potassium minerals. Because of the similarity of the ionic size of K^+ and Pb^{2+} ions, it appears reasonable to assume that Pb^{2+} ions, at least in some degree, are able to occupy positions identical with the positions of the K^+ ions in the structures of potassium minerals.

The substitution of potassium by lead evidently takes place in the feldspars. Both potash feldspar and lead feldspar are known as natural or artificial compounds. They have similar crystal structures, in which the K^+ and Pb^{2+} ions occupy identical positions. Therefore, natural potash feldspars, which contain only minute quantities of lead, may also be considered to be isomorphic mixtures of the compounds $KAlSi_3O_8$ and $PbAl_2Si_2O_8$, with lead replacing potassium in random distribution. A lead mica, corresponding to potash micas, however, neither has been prepared artificially nor occurs in Nature, and therefore its crystal structure is unknown. A survey of the properties of the Pb^{2+} ion, compared with those of the K^+ ion and the example given by the feldspars, makes it highly probable that in the micas the manner of occurrence of lead is also controlled by a similar replacement.

The geochemical relationship between lead and potassium shows that the atomic arrangement in mineral structures and the properties of the individual atoms or ions are pertinent to geochemical phenom-

ena in the upper lithosphere. This manner of reasoning, which may be called atomic, is important in geochemical research of crystalline substances.

Some principles dealing with the structure of crystals and with the properties of their constituents will be briefly reviewed in the subsequent paragraphs. With reference to the laws governing the atomic arrangement in crystals and to the properties of crystal structures, the reader is referred to well-known treatises, e.g., Bragg (1937), Bragg and Bragg (1939), Evans (1939), Pauling (1945), Seitz (1940), Stillwell (1938), Wells (1945). In the next few paragraphs only the more important applications of crystal chemistry to geochemistry will be considered, and no attempt will be made to present an exhaustive discussion.

PARTICLE SIZE

In crystal chemistry it is customary to consider the size of the particles constituting the crystals, viz., the atoms and ions. Because the neutral atoms and the electrically charged ions are not strictly limited bodies, their size merely shows their space requirements in the structures. The space required by a particle is controlled by the equilibrium between the attractive and the repulsive forces acting between two neighboring particles. The distance at which attraction and repulsion are in equilibrium is defined as the sum of the radii of the two particles. By determining the distances between the particles in simple compounds in which the closest neighbors may be considered to contact one another, it is possible to obtain a general picture of the effective particle sizes in all compounds. The division of the distance between two neighboring particles, in order to get the values of the length of their radii, is more or less arbitrary from a physical viewpoint. However, the radii obtained are very useful in geochemistry and will be used throughout this book.

The effective size of an atom or an ion in a structure, i.e., its atomic or ionic radius, depends on the nature of the binding forces between neighboring particles, on the electronic configuration of the atom or the ion, on the polarization properties of the particle, and on its coordination, i.e., on the number and arrangement of the neighboring particles. The atomic and ionic radii of the elements are given in Appendix 3, and the electronic structure of the elements is presented in Appendix 4.

The ionic bond predominates in the structures of the petrologically most important minerals. Actually, for geochemical purposes, it is

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adequate to consider the structures of the feldspars, pyroxenes, amphiboles, micas, and a number of other minerals as essentially ionic. However, it must be borne in mind that in some other minerals, e.g., in the sulfides, the structure deviates very considerably from an ionic structure, and therefore the ionic radii cannot be applied to such structures. Because several factors affect the ionic radii, the values listed in Appendix 3 are not strictly valid for the structures of all minerals but must be corrected to comply with the circumstances prevailing in the various structures. The reason for giving all ionic radii for a 6-fold co-ordination of the sodium chloride type is to make them comparable with one another.

The relationship between the magnitude of the ionic radii of the elements and their position in the Periodic System is of fundamental importance in geochemistry. To illustrate the relationship, a part of the Periodic System and the ionic radii of the elements in question are presented in Table 5.5. For polyvalent elements, only the radius corresponding to the valence given at the head of the column is indicated.

The mechanism of ionization clearly shows that the size of the ionic radius decreases regularly in each period when passing from the left to the right. This rule is valid for ions with a similar population of the outermost electron shell and with regularly increasing positive charge. An illustrative example is the series Na^+ - Mg^{2+} - Al^{3+} - Si^{4+} - P^{5+} - S^{6+} .

In the vertical columns of Table 5.5 the ionic radius increases when passing down toward the higher atomic numbers. An illustrative example of this rule is the series Be^{2+} - Mg^{2+} - Ca^{2+} - Sr^{2+} - Ba^{2+} - Ra^{2+} , in which the outermost electron shell also is equally populated by electrons. Unlike the series Na^+ - S^{6+} , in the Be^{2+} - Ra^{2+} series all ions are equally charged. It may be stated, in general, that, if the ionic charge and the population of the outermost electron shell remain unchanged, the ionic radius increases with increasing atomic number. This rule is understood on the basis of the fact that new shells become populated by electrons when passing from ions of low atomic number to those with high atomic number.

There is a remarkable exception to the above rule, viz., the elements from lanthanum ($Z = 57$) to lutecium ($Z = 71$), or the series of the lanthanides. The radii of the trivalent ions of these metals decrease pronouncedly in size with increasing atomic number. The decrease is illustrated in Table 5.6. As is well known,

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this peculiarity is the consequence of the addition of new electrons to the inner shells in the lanthanide series. The decrease of the ionic radius is caused by the increase of nuclear charge and by the correspondingly increasing attraction on the electrons.

The decrease of the size of the ionic radius in the lanthanide series is called the lanthanide contraction and is of considerable geochemi-

TABLE 5.5
RADII OF SOME IONS (IN kX) IN PART OF THE PERIODIC SYSTEM

CHARGE OF ION					
1+	2+	3+	4+	5+	6+
Li 0.78	Be 0.34	B 0.20	C 0.19	N 0.1-0.2	
Na 0.98	Mg 0.78	Al 0.57	Si 0.39	P 0.35	S 0.34
K 1.33	Ca 1.06	Sc 0.83	Ti 0.64	V ~0.4	Cr 0.3-0.4
Cu 0.96	Zn 0.83	Ga 0.62	Ge 0.44	As 0.40	Se 0.3-0.4
Rb 1.49	Sr 1.27	Y 1.06	Zr 0.87	Cb 0.69	Mo 0.67
Ag 1.13	Cd 1.03	In 0.92	Sn 0.74	Sb 0.62	
Cs 1.65	Ba 1.43	La 1.22	Hf 0.84	Ta 0.68	
Au 1.37	Hg 1.12	Tl 1.05	Pb 0.84	Bi 0.74	
	Ra 1.52				

cal importance. The effect of the increasing nuclear charge on the ionic radius is relatively small compared with the corresponding effect of, e.g., increasing ionic charge resulting from the removal of an electron. Therefore, the total decrease in the size of the ionic radius in the lanthanide series of fifteen elements is remarkably small. Moreover, the lanthanides, because of the unchanged population of the outermost electron shell throughout the whole series, are chemically very similar. The similarity in chemical properties and in space requirements in crystal structures makes the lanthanides a very coherent group of elements (see chap. 18).

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The lanthanide contraction affects the geochemistry not only of the lanthanides but also of the elements following them in the Periodic System, viz., those with atomic numbers greater than 71. Table 5.7 is presented to illustrate the effect of the lanthanide contraction on the size of the ionic radii of the heaviest elements in the Periodic System. In this table the ionic radii of the alkali metals and of the copper group (Cu, Ag, Au) are taken as the unit, and the ionic radii of the elements occurring in the same periods are correspondingly reduced. Thus, e.g., the figure for Mg is the radius ratio of Mg^{2+} to Na^+ , or 0.78 kX:0.98 kX, or 0.80, and for Sn the radius ratio of Sn^{4+}

TABLE 5.6
IONIC RADII OF THE TRIVALENT LANTHANIDES

Atomic No. <i>Z</i>	Element	Symbol	Ionic Radius in kX
57	Lanthanum	La	1.92
58	Cerium	Ce	1.18
59	Praseodymium	Pr	1.16
60	Neodymium	Nd	1.15
61	Promethium	Pm	
62	Samarium	Sm	1.13
63	Europium	Eu	1.13
64	Gadolinium	Gd	1.11
65	Terbium	Tb	1.09
66	Dysprosium	Dy	1.07
67	Holmium	Ho	1.05
68	Erbium	Er	1.04
69	Thulium	Tm	1.04
70	Ytterbium	Yb	1.00
71	Lutecium	Lu	0.99

to Ag^+ is 0.74 kX:1.13 kX, or 0.65. The figures in Table 5.7, calculated from the ionic radii given in Appendix 3, indicate the ratio of the ionic radius of an element in the first group to that of an element in the same period. The ratios illustrate the decrease in the size of the ionic radius which results from an increase in the nuclear charge and in the ionic charge and allow a comparison of the magnitude of the decrease in the different periods.

In the vertical columns of Table 5.7, e.g., in the series Be-Ba and Zn-Cd, the calculated ratios show an increase until the lanthanide contraction becomes effective between lanthanum and hafnium. The simultaneous increase in the nuclear charge and in the ionic charge by one unit evidently has no very marked effect on the ionic radii of elements with high atomic number. Beginning with hafnium, the ratio decreases, apparently because of the lanthanide contraction.

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This decrease indicates that the ionic radii of elements with higher atomic number than 71 (lutecium) are smaller than they would be if the lanthanide contraction did not occur. This result may already have been expected from a survey of the ionic radii listed in Table 5.5; and Table 5.7 further elucidates the contraction.

TABLE 5.7
EFFECT OF LANTHANIDE CONTRACTION ON IONIC
RADII OF HEAVIEST ELEMENTS
OF PERIODIC SYSTEM

CHARGE OF ION				
1+	2+	3+	4+	5+
Li 1	Be 0 44	B 0 26		
Na 1	Mg 0 80	Al 0 58	Si 0 40	P 0 36
K 1	Ca 0 80	Sc 0 62	Ti 0 48	V ~0 3
Cu 1	Zn 0 86	Ga 0 65	Ge 0 46	As 0 42
Rb 1	Sr 0 86	Y 0 71	Zr 0 58	Cb 0 46
Ag 1	Cd 0 91	In 0 81	Sn 0 65	Sb 0 55
Cs 1	Ba 0 87	La 0 74	Hf 0 51	Ta 0 41
Au 1	Hg 0 82	Tl 0 77	Pb 0 61	Bi 0 54

The effect of the lanthanide contraction on the geochemistry of the heaviest elements of the Periodic System is remarkably well illustrated by the manner of occurrence of hafnium, the next element to follow after the lanthanides. Owing to the contraction, the ionic radii of hafnium and zirconium are very similar. The similarity in the space requirement of their ions, along with their close chemical similarity, makes hafnium and zirconium geochemically a very coherent pair of elements. Hafnium always follows zirconium in Nature. The geochemical coherence between hafnium and zirconium is decidedly more pronounced than is the coherence in the corresponding pairs of elements that precede the lanthanides, viz., La-Y, Ba-Sr, and Cs-Rb.

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Without the lanthanide contraction, however, the ionic radius of hafnium would be considerably greater than the ionic radius of zirconium. If this were the case, the coherence between hafnium and zirconium probably would be less pronounced, and hafnium evidently would, geochemically, be an independent element.

Tantalum, the next element after hafnium in the Periodic System, has an ionic radius very similar to the ionic radius of its lower homologue, columbium. In fact, tantalum and columbium are geochemically very closely related, although their relationship is less pronounced than that of hafnium and zirconium. It is highly probable that, without the lanthanide contraction, the relationship between tantalum and columbium would be less close. The geochemical coherence in the next pair to follow tantalum and columbium, viz., tungsten and molybdenum, is remarkable in oxygen-bearing compounds of the two metals, but it is definitely weaker than the coherence in the pair tantalum-columbium.

The effect of the lanthanide contraction on geochemical relationships between elements in the fourth, fifth, and sixth periods of the Periodic System is illustrated by the radius ratios given in Table 5.8, in which the figure between K and Rb, for example, indicates the radius ratio of Rb^+ to K^+ , which is $1.49 \text{ kX} : 1.33 \text{ kX}$, or 1.12. In a similar manner the figure between Rb and Cs indicates the radius ratio of Cs^+ to Rb^+ , viz., $1.65 \text{ kX} : 1.49 \text{ kX}$, or 1.11. When the elements of the fourth and fifth period are compared with one another, a decrease in geochemical coherence becomes apparent when passing from the left to the right. Rubidium is very closely related to potassium; in fact, their relationship is so close that rubidium does not form any independent minerals but always occurs concealed in potash minerals. Strontium occurs frequently in calcium minerals and forms a great number of independent minerals, particularly in hydrothermal deposits. Moreover, strontium is found in potassium minerals. The geochemical coherence of yttrium and scandium is remarkable but weaker than the coherence of strontium and calcium. The pairs zirconium-titanium and columbium-vanadium show but slight parallelism in their manner of occurrence. Molybdenum and chromium are geochemically almost unrelated to each other if only the oxygen-bearing compounds of Mo^{6+} and Cr^{6+} are considered. The geochemical relationships of the elements belonging to the fifth and sixth periods are similar until the lanthanides are reached. Cesium and rubidium are closely related to each other, even though they

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probably are somewhat less coherent than rubidium and potassium. Sometimes cesium forms an independent mineral, viz., pollucite, in which rubidium and potassium are present only as minor constituents. Barium and strontium are decidedly less related to each other than are cesium and rubidium. The relationship between lanthanum and yttrium is approximately similar to that between yttrium and scandium. Between lanthanum and hafnium there is an abrupt break in geochemical coherence. In contrast to the relatively weak relationship between zirconium and titanium, hafnium and zirconium form a highly coherent pair. The coherence in the pair tantalum-columbium is far more pronounced than the coherence in the pair columbium-

TABLE 5.8

GEOCHEMICAL RELATIONSHIP BETWEEN ELEMENTS OF FOURTH, FIFTH,
AND SIXTH PERIOD OF PERIODIC SYSTEM AS AFFECTED
BY LANTHANIDE CONTRACTION

PERIOD	CHARGE OF ION					
	1+	2+	3+	4+	5+	6+
Fourth.....	K 1.12	Ca 1.20	Sc 1.28	Ti 1.36	V 1.4-1.7	Cr 1.6-2.2
Fifth.....	Rb 1.11	Sr 1.13	Y 1.15	Zr 0.97	Cb 0.99	Mo
Sixth.....	Cs	Ba	La	Hf	Ta	

vanadium but is weaker than in the pair hafnium-zirconium. In contrast to the pair molybdenum-chromium, the pair tungsten-molybdenum shows a remarkable parallelism in the manner of the occurrence of W^{6+} and Mo^{6+} ions in oxygen-bearing compounds. The coherence relationships discussed above agree with the radius ratios given in Table 5.8.

The influence of the lanthanide contraction on the geochemistry of the series Au-Hg-Tl-Pb-Bi is less pronounced. This is partly the result of the fact that some of these elements occur very characteristically in minerals which have essentially nonionic structures. Furthermore, it is evident that the immediate effect of the lanthanide contraction on the ionic radius will diminish in the direction from hafnium toward higher atomic numbers.

A similar contraction exists elsewhere in the Periodic System, viz., the contraction which starts with actinium. It is called the actinide contraction and is illustrated by the ionic radii listed in Table 5.9,

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according to Zachariasen (1948). The radii given in this table are based on the value of 1.40 kX for the radius of the O^{2-} ion and consequently are not comparable with the values given in Appendix 3. The geochemical importance of the actinide contraction is limited to the elements of the actinide series. It explains the relationship between thorium and uranium in some minerals.

Along with the lanthanide and actinide contraction, another peculiarity in the experimentally determined ionic radii must be mentioned, viz., the abnormally great ionic radius of lithium. Careful consideration of the radii and of their ratios presented in Tables 5.5 and 5.7 shows that the radius of the Li^+ ion is greater than the regular change in the size of the ionic radius in the Periodic System would

TABLE 5.9
CRYSTAL RADIUS OF THE TRIVALENT ACTINIDES

Atomic No. <i>Z</i>	Element	Symbol	Crystal Radius in kX
89.....	Actinium	Ac	1.11
90.....	Thorium	Th	(1.08)
91.....	Protactinium	Pa	(1.06)
92.....	Uranium	U	1.04
93.....	Neptunium	Np	1.02
94.....	Plutonium	Pu	1.01
95.....	Americium	Am	1.00

suggest. This is clearly shown by the low radius ratio of beryllium to boron in Table 5.7, compared with the considerably higher ratio of magnesium to aluminum. The exceptionally high value of the radius of Li^+ is shown in Figure 5.1, which illustrates the increase of the size of the ionic radius in the three series Li-Na-K-Rb-Cs, Be-Mg-Ca-Sr-Ba-Ra, and B-Al-Sc-Y-La. In the two last-mentioned series the curve is smooth, but lithium causes a jump in the curve of the alkali metals. The great radius of Li^+ is important in the geochemistry of lithium and explains the substitution of magnesium by lithium in many silicate minerals.

CO-ORDINATION OF THE PARTICLES

The structural constituents of a crystal, viz., molecules, neutral atoms, or electrically charged ions, are arranged to give their system the minimum amount of potential energy. Such an arrangement evidently requires a relatively high degree of order, with due consideration to the more or less strictly fixed positions of the particles.

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In the structure of a crystalline mineral, each particle (*A*) is surrounded by a number of particles of another kind (*B*). The number and arrangement of the particles (*B*) which are the nearest neighbors of the particle (*A*) indicates the co-ordination of particle (*A*) with respect to particle (*B*). The co-ordination is different for different particles and for different structures; evidently it is the most fundamental feature of the structure. Each particle obviously tends to occupy the co-ordination into which it fits best. The properties of the particle, e.g., its space requirements, electrostatic charge, polarizability, and polarizing power, make one co-ordination more suitable

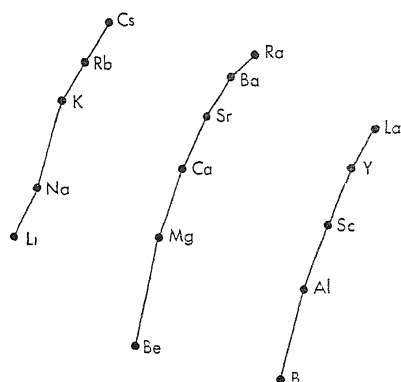


FIG. 5.1.—Change of the size of ionic radius of some elements in Groups I, II, and III of the Periodic System.

than another. The better the particle fits into a co-ordination, the more strongly it is linked to the surrounding structure and the higher is the energy barrier which must be overcome before the particle can move into another co-ordination or leave the structure altogether. This principle, simple and self-evident as it may sound, is of considerable importance in geochemistry, and several examples of its application will be found on the later pages of this book. Only two examples will be mentioned here, both of which will be discussed more thoroughly in forthcoming paragraphs and chapters, that is, the non-existence of a lithium feldspar and the incidental disintegration of the zircon structure. In contrast to all other alkali metals, lithium does not form the stable compound $\text{Li}[\text{AlSi}_3\text{O}_8]$ with feldspar structure. The nonexistence of this compound is understood on the basis

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of a co-ordination which is unsuitable for lithium in the feldspar structure. The force required to remove the lithium ion from the feldspar structure is too weak to allow the formation of a stable atomic arrangement of the feldspar type. In a similar manner the co-ordination of the zirconium ion in the zircon structure is not well suited to the space required by the Zr^{4+} ion. Therefore, a relatively weak force, e.g., a radioactive impulse, will be sufficient to break down the zircon structure and cause a metamict disintegration sometimes found in this mineral.

The two examples illustrate the relationship between the stability of a structure and the co-ordination of its particles. Evidently, the total stability of the structure is controlled by the strength of the weakest bond, which cannot be broken without causing the collapse

TABLE 5.10
RADIUS RATIO OF ANION TO CATION FOR DIFFERENT CO-ORDINATIONS

Co-ordination No of Cation	Arrangement of Anions around Cation	Radius Ratio Cation: Anion
2.....	Opposite one another	Up to 0.15
3.....	Corners of an equilateral triangle	0.15-0.22
4.....	Corners of a tetrahedron	0.22-0.41
6.....	Corners of an octahedron	0.41-0.73
8.....	Corners of a cube	> 0.73

of the structure. Through thermal or other agitation the weakest bond will be severed first, and consequently it will determine the degree of stability of the whole structure.

The co-ordination of a cation, i.e., the number and arrangement of anions surrounding the cation in an essentially ionic structure, largely depends on the cation:anion radius ratio. The relationship between the co-ordination and the relative size of the particles is reviewed in Table 5.10. The figures for the radius ratio were calculated from the assumption that the ions are rigid spheres in contact with one another. Consequently, the figures are not strictly applicable to structures composed of ionized atoms. They may, however, be used as an approximate basis for the following discussion. Table 5.10 shows that, with increasing radius ratio, the co-ordination number increases in the manner indicated.

The close relationship between particle size and co-ordination in a crystal structure requires careful consideration of the radii of the cations and of the anions. In the petrologically most important min-

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erals, oxygen is the principal anion. Table 2.2 shows the abundance of the eight main constituents of igneous rocks, calculated in percentages by volume. The igneous rocks contain about 92 per cent oxygen by volume. This result, explained by the high abundance of oxygen and by its great ionic size, compared with the size of most cations, illustrates the high importance of oxygen in the mineral structures. The crystalline oxygen-bearing minerals are actually aggregates of big oxygen ions whose interstices in the structures are filled by the cations. This circumstance is illustrated by the composition by volume of some important rock-making minerals, given in Table 5.11.

TABLE 5.11
COMPOSITION OF SOME ROCK-MAKING MINERALS IN PER CENT BY VOLUME

Element	Potash Feldspar K[AlSi ₃ O ₈]	Albite Na[AlSi ₃ O ₈]	Anorthite Ca[Al ₂ Si ₂ O ₈]	Quartz SiO ₂	Diopside CaMg[Si ₂ O ₆]	Muscovite KAl ₂ [(OH) ₂ [AlSi ₃ O ₁₀]]
O.....	87.1	93.3	91.6	98.7	88.6	89.9
K.....	11.1					7.6
Na.....		4.8				
Ca.....			5.9		7.6	
Si.....	0.9	0.9	0.6	1.3	0.8	0.6
Al.....	0.9	1.0	1.9			1.9
Mg.....					3.0	
Total	100.0	100.0	100.0	100.0	100.0	100.0

The fact that oxygen forms the skeleton of most of the petrologically and geochemically important minerals justifies special consideration of the cation:oxygen radius ratio. Based on the values given in Appendix 3, these ratios, for a number of cations, are presented in Table 5.12.

The first column of the table, with the radius ratio less than 0.22, includes only N⁵⁺, C⁴⁺, and B³⁺. In fact, nitrogen and carbon are 3-co-ordinated in the NO₃⁻ and CO₃²⁻ groups of nitrates and carbonates. Boron is a transition element between 3- and 4-co-ordination in mineral structures. In borates it forms BO₃⁻ groups. In some artificial borates the BO₃⁻ groups are linked together by common oxygen atoms and give rise to structural variations similar to those which occur in silicates. The crystal structures of the natural borates are very incompletely known, and therefore the existence of independent B₂O₄²⁻ groups, infinite BO₂ chains, etc., in the natural borates is still unknown. The crystal chemistry of boron resembles, to a certain extent, the crystal chemistry of silicon, and therefore the natural

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borates might be comparable to the natural silicates. Along with the 3-co-ordinated boron of the borates, 4-co-ordinated boron is present in the borosilicates, such as danburite, $\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$. It is probable that, when boron occurs as an accessory constituent of silicate structures, it is partly 3- and partly 4-co-ordinated. Hamburger and Buerger (1948) showed that tourmaline, the most abundant boriferous mineral, contains boron in 3-co-ordination with respect to oxygen.

TABLE 5.12
RADIUS RATIOS OXYGEN : CATION FOR SOME IONS

RADIUS RATIO, $r_{\text{OXYGEN}} : r_{\text{CATION}}$							
< 0.22		0.22-0.41		0.41-0.71		> 0.71	
N ⁵⁺	0.08-0.15	Cr ⁶⁺	0.23-0.30	Al ³⁺	0.43	Cu ⁺	0.73
C ⁴⁺	0.14	Be ²⁺	0.26	Ga ³⁺	0.47	Na ⁺	0.74
B ³⁺	0.15	P ⁶⁺	0.27	Cr ³⁺	0.48	Cd ²⁺	0.78
		V ⁵⁺	~ 0.3	Ti ⁴⁺	0.48	Ca ²⁺	0.80
		Si ⁴⁺	0.30	V ³⁺	0.49	Y ³⁺	0.80
		As ⁵⁺	0.30	Mo ⁶⁺	0.51	Hg ²⁺	0.85
		Ge ⁴⁺	0.33	Fe ³⁺	0.51	La ³⁺	0.92
		Mn ⁴⁺	0.39	Cb ⁵⁺	0.52	Sr ²⁺	0.96
				Ta ⁵⁺	0.52	Pb ²⁺	1.00
				Mn ³⁺	0.53	K ⁺	1.01
				Sn ⁴⁺	0.56	Ba ²⁺	1.08
				Li ⁺	0.59	Rb ⁺	1.13
				Mg ²⁺	0.59	Tl ⁺	1.13
				Ni ²⁺	0.59	Cs ⁺	1.25
				Co ²⁺	0.62		
				Fe ²⁺	0.63		
				Sc ³⁺	0.63		
				Zn ²⁺	0.63		
				Hf ⁴⁺	0.64		
				Pb ⁴⁺	0.64		
				Zr ⁴⁺	0.66		
				Mn ²⁺	0.69		
				In ³⁺	0.70		

In accordance with the predictions of Table 5.10, the ions listed in the second column of Table 5.12 are exclusively 4-co-ordinated in oxygen-bearing minerals—Mn⁴⁺ is the only exception to this rule. It lies close to the upper limit of the radius ratio of the 4-co-ordinated ions and it is 6-co-ordinated in MnO₂.

The ions listed in the third column of Table 5.12 are 6-co-ordinated in oxygen-bearing structures. However, there are some characteristic exceptions. The radius of Al³⁺ is close to the lower limit indicated at the head of the third column. As a matter of fact, aluminum is able to occur both in a 4-fold and in a 6-fold co-ordination. In the feld-

spars, aluminum is tetrahedrally co-ordinated. Because the feldspars are the most important aluminum-bearing minerals, it is evident that the greatest part of the aluminum in the rocks of the lithosphere is tetrahedrally co-ordinated. The co-ordination number 4 is consequently more abundant for aluminum than is the number 6. In independent minerals, sexvalent molybdenum and bivalent zinc are preferentially 4-co-ordinated. This is particularly remarkable in the case of zinc, which has a fairly great ionic radius. Silicate minerals containing zinc in 4-co-ordination include, among others, willemite, $\text{Zn}_2[\text{SiO}_4]$, and hemimorphite, $\text{Zn}_4[(\text{OH})_2[\text{Si}_2\text{O}_7] \cdot \text{H}_2\text{O}]$. Quadrivalent zirconium occurs in 8-co-ordination in zircon, which is the most abundant zirconium mineral. Many of the ions listed in the third column may occur in a 4-fold or in an 8-fold co-ordination in certain minerals.

Transitional ions between the third and fourth columns in Table 5.12 include, among the more common ions, Na^+ and Mn^{2+} . They both occur in a 6-fold or higher co-ordination. The cations with a greater radius than the radius of Na^+ mostly have co-ordination numbers greater than 6.

The relationship between the ionic size and the co-ordination number with respect to oxygen is diagrammatically illustrated in Figure 5.2, in which the various cations, arranged according to their size, are plotted against co-ordination number. The black areas in the figure indicate roughly the abundance of the co-ordinations of the ions in the upper lithosphere. For the largest ions the black area is wider than for the small ions. This illustrates the fact that the cation's co-ordination number is less definite because of its great size.

STRUCTURAL CLASSIFICATION OF SILICATE MINERALS

In almost all modern handbooks of mineralogy the basis of the classification of minerals is the crystal structure, which is already known for most of the important minerals. A structural classification of the complicated silicate minerals is particularly useful. For the silicates the type of linkage of the silicon-oxygen tetrahedra forms a natural background of classification, the one presented by Strunz (1941) being adopted for this book. The formulas of the silicates and of other minerals are written in the form suggested by Strunz, inasmuch as they represent, thus far, the only systematic attempt to show structural features in the formula of a mineral. It is well understood that a formula cannot be more than a schematic

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expression of the structural features which are decisive in giving a mineral the right place in a natural system of minerals. The type of crystal structure of a mineral is often as important for geochemical purposes as is its bulk chemical composition. Therefore, it is desirable to give the formula of a mineral some structural features. According to Strunz, the complex framework (Si-O, Si-Al, etc.) of the structure

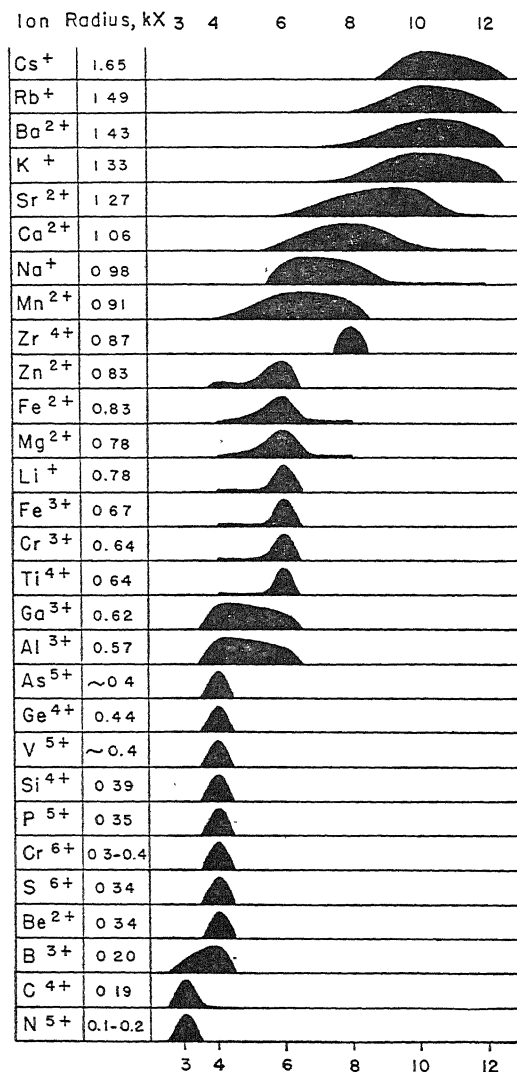


FIG. 5.2.—The co-ordination number with respect to oxygen of some geochemically important cations in the upper lithosphere.

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is given in brackets: []. The groups OH, F, O, etc., which are not linked to silicon atoms, are given in the brackets but are separated from the framework by a vertical line: |. The cations lying outside the framework are beyond the brackets in the formula. A general scheme of the structural classification of silicate minerals is presented in Table 5.13.

TABLE 5.13
STRUCTURAL CLASSIFICATION OF SILICATE MINERALS

Group	Manner of Linkage of Silicon-Oxygen Tetrahedra	Examples
Nesosilicates (<i>νησος</i> = island)	Separate $[\text{SiO}_4]$ "islands," which do not share any oxygen atoms with the neighboring silicon-oxygen tetrahedra; the silicates belonging to this group are orthosilicates in the proper sense of the word	Forsterite $\text{Mg}_2[\text{SiO}_4]$ Grossularite $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$ Andalusite $\text{Al}_2\text{O}[\text{SiO}_4]$
Sorosilicates (<i>σωρός</i> = group)	Separate groups of silicon-oxygen tetrahedra, sharing one or more corners with neighboring tetrahedra of the same group; the following subgroups may be distinguished:	
	(1) $[\text{Si}_2\text{O}_7]$ double tetrahedra	Thortveitite $\text{Sc}_2[\text{Si}_2\text{O}_7]$ Hemimorphite $\text{Zn}_4[(\text{OH})_2 \text{Si}_2\text{O}_7] \cdot \text{H}_2\text{O}$
	(2) Five tetrahedra in an open group	Zunyite $\text{Al}_{12}[\text{AlO}_4]_5(\text{OH}, \text{F})_{15}\text{Cl} \text{Si}_5\text{O}_{16}]$
	(3) Rings of three tetrahedra	Wollastonite $\text{Ca}_3[\text{Si}_3\text{O}_9]$ Benitoite $\text{BaTi}[\text{Si}_3\text{O}_9]$
	(4) Rings of six tetrahedra	Beryl $\text{Al}_2\text{Be}_3[\text{Si}_6\text{O}_{18}]$ Cordierite $\text{Mg}_2\text{Al}_2[\text{AlSi}_5\text{O}_{18}]$
Inosilicates (<i>ις, ινός</i> = fiber)	Infinite chains or double chains of silicon-oxygen tetrahedra	Sillimanite $\text{Al}[\text{AlSiO}_5]$ Pyroxenes Amphiboles
Phyllosilicates (<i>φύλλον</i> = leaf)	Infinite sheets of silicon-oxygen tetrahedra	Talc $\text{Mg}_3[(\text{OH})_2 \text{Si}_4\text{O}_{10}]$ Micas Kaolinite $\text{Al}_4[(\text{OH})_8 \text{Si}_4\text{O}_{10}]$
Tectosilicates (<i>τεκτονεία</i> = framework)	Continuous frameworks of linked tetrahedra, sharing all four oxygen atoms with the neighboring tetrahedra	Feldspars Feldspathoids Zeolites

ISOMORPHISM AND DIADOCHY

Minerals are rarely pure compounds. Analyses made of even the chemically simple minerals reveal, as a rule, a chemical composition deviating more or less from the ideal composition presented in the handbooks. The deviation might be caused partly by defects in the structure (vacant positions, etc.). As a matter of fact, structural deficiency is apparently a very common phenomenon. A well-known example is pyrrhotite, in which vacant positions of Fe^{2+} ions partly occupied by Fe^{3+} cause an excess of sulfur over that expressed by the formula FeS . However, the main reason for the deviation is that most minerals are capable of incorporating various elements as impurities. The impurities may occur as mechanically admixed inclusions or may occupy fixed positions in the structure or be inclosed in the empty spaces therein.

According to common mineralogical usage, the foreign material is said to be present in solid solution in the mineral. The term solid solution between a solute (A) and a solvent (B) merely indicates that the material is homogeneous. By means of microscopic or X-ray investigation, only one phase (AB) is detectable. The term solid solution states nothing about the structural manner of occurrence of the solute in the solvent. Consequently, two structurally different kinds of solid solutions may be distinguished.

1. The solute is completely beyond the structural framework of the solvent and does not participate in its binding. Probably one of the most typical examples of a solid solution of this kind is the occurrence of helium or cesium in beryl. Atoms of these elements are sometimes found in the beryl structure within the six-rings of $[\text{SiO}_4]$ tetrahedra. The two elements do not belong to their host structure.

2. The solute forms a complete isomorphic series with the solvent. An illustrative example is ferrous orthosilicate (fayalite) in magnesium orthosilicate (forsterite). The Fe^{2+} ions replace the Mg^{2+} ions in random distribution and therefore occupy their structural positions.

Between the two extremes all intermediate types of solid solutions occur in minerals. The terminology applied to the different types in literature is not completely uniform, particularly with the terms isomorphism and isomorphic mixture. Because isomorphism and related phenomena are of very high importance in geochemistry, it appears pertinent to define the terminology adopted in this book. The definitions given below are those of Strunz (1936, 1937).

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Two compounds, (*A*) and (*B*), are called isomorphic if the following requirements are fulfilled:

1. The structures of the two compounds must be of a similar type, with closely similar positions of the atoms. The lengths of the axes of the unit cell of (*A*) must be closely similar to those of (*B*) or to their integer multiples.

2. The cation:anion radius ratios in the two compounds must be close to each other.

3. The compound (*A*) must be able to incorporate more than about 5 per cent of the compound (*B*) in solid solution, and vice versa. The requirement of an actual formation of mixed crystals corresponds to the original definition of isomorphism given by Eilhard Mitscherlich in 1821.

The isomorphism thus defined may be complete or partial, passing over to isotypy. For two compounds isotypic with each other the first requirement of isomorphism must be fulfilled. The cation:anion radius ratios in the two compounds differ considerably from each other. Because of this difference, the compound (*A*) cannot contain more than about 5 per cent of the compound (*B*) in solid solution, and vice versa. When present in the same rock, the two compounds do not form mixed crystals but separate as independent phases. Zircon, $\text{Zr}[\text{SiO}_4]$, and xenotime, $\text{Y}[\text{PO}_4]$, are examples of isotypic minerals.

Originally, the terms isomorphic and isotypic referred to the crystalline compounds as a whole. However, if, instead of the compounds, only some elements contained therein are considered, the terms lose their significance. In geochemistry it is often preferable to consider atoms or ions and their mutual relationships in the structures of minerals instead of the minerals themselves. Therefore, according to the suggestion made by Paul Niggli and published by Strunz (1937), two atoms or ions occurring in a mineral are called diadochic if they are capable of replacing each other in the structure of the mineral, each occupying the other's position. Consequently, e.g., forsterite and fayalite are isomorphic, but the Fe^{2+} and Mg^{2+} ions in their structures are diadochic. It must be emphasized that the concept of diadochy always refers to a given structure; in other words, two elements may be diadochic in one mineral and not diadochic in another mineral. The concept of diadochy includes the actual replaceability in the structure, and diadochy may be complete or partial. The substitution is primarily regulated by the space re-

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quirements of the atoms or ions of the two elements in question. Generally speaking, it may be stated that the ion (*A*) may replace the ion (*B*) diadochically if the difference in the size of their radii does not exceed about 15 per cent of the radius of (*B*). However, this rule is not always valid; it is merely a rough approximation that gives some idea of the magnitude of the difference allowed.

Along with the space requirements of the two ions replacing each other, temperature affects the degree of diadochy. High temperature usually favors diadochic substitution. This is well illustrated by the salt minerals of the evaporates, as compared with the minerals of the igneous rocks (see under "Evaporates," p. 218). The salt minerals of the evaporates crystallize from an aqueous solution and form at a temperature very much lower than those of crystallizing magmas. The salts of the common alkali metals found in the evaporates are either potassium compounds, sodium compounds, or, in some cases, double salts in which potassium and sodium do not occupy identical positions in the structure (e.g., glaserite or apthitalite, $\text{NaK}_3[\text{SO}_4]_2$) and consequently are not diadochic with one another. The potassium compounds are, as a rule, remarkably devoid of sodium, and vice versa. On the other hand, among the alkali minerals of the igneous rocks, potash feldspar and soda feldspar, which are very abundant, seldom, if ever, are purely potassic or purely sodic minerals. They are mostly isomorphic mixtures of the compounds $\text{K}[\text{AlSi}_3\text{O}_8]$ and $\text{Na}[\text{AlSi}_3\text{O}_8]$, in which potassium and sodium replace each other in random distribution. All petrographic experience favors the conclusion that the two feldspars are completely isomorphic only at elevated temperatures. With decreasing temperature, exsolution takes place and causes the formation of the perthitic structure common in the alkali feldspars of igneous rocks. It is not known whether the exsolution in natural alkali feldspars results in the formation of phases consisting of pure potash and soda components or whether the exsolved potash component still carries considerable quantities of soda, and vice versa. Information on the chemical composition of the potash and soda phases of perthitic alkali feldspars and experimental investigation of the mix-crystals of $\text{K}[\text{AlSi}_3\text{O}_8]$ and $\text{Na}[\text{AlSi}_3\text{O}_8]$ probably would add to the knowledge of the mechanism of the formation of perthite. Like the sodium-potassium diadochy of the alkali feldspars, probably the sodium-calcium diadochy of the plagioclases also depends on temperature.

The clay minerals afford another example of the dependence of

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diadochy on temperature (see under "Hydrolyzates," p. 202). Their sheetlike structures, evidently formed at low temperatures, are related to the structures of micas of igneous rocks. As in the feldspars, aluminum in the micas partly replaces silicon diadochically in 4-co-ordination. Along with the tetrahedrally co-ordinated aluminum, most micas also contain octahedrally co-ordinated aluminum that forms bridges between the neighboring sheets of tetrahedra. The low temperature of formation of the clay minerals evidently prevents the presence of 4-co-ordinated aluminum. Most clay minerals contain aluminum exclusively in 6-co-ordination between two adjacent sheets of tetrahedra.

TABLE 5.14
IONIZATION POTENTIAL OF SOME IONS IN eV

Ion	Ionization Potential	Ion	Ionization Potential	Difference (Per Cent)
Si ⁴⁺	44.89	Ge ⁴⁺	45.5	1
K ⁺	4.339	Rb ⁺	4.176	4
Fe ²⁺	16.16	Co ²⁺	17.3	7
Mg ²⁺	14.96	Fe ²⁺	16.16	8
Al ³⁺	28.31	Ga ³⁺	~30.6	8
Fe ²⁺	16.16	Zn ²⁺	17.89	11
Fe ²⁺	16.16	Ni ²⁺	18.2	13
Mg ²⁺	14.96	Co ²⁺	17.3	16
Mg ²⁺	14.96	Zn ²⁺	17.89	20
Mg ²⁺	14.96	Ni ²⁺	18.2	22
Rb ⁺	4.176	Tl ⁺	6.106	32
Na ⁺	5.138	Cu ⁺	7.723	50

Goldschmidt (1937a) discussed the influence of ionization potential on the diadochy between elements with the same ionic charge and with closely similar ionic radii. He pointed out that some elements occupying identical positions in the structures of minerals and therefore being geochemically closely related have similar ionization potentials. In Table 5.14 several ionic pairs, with similar charge and similar radius, are compared with one another. They are arranged according to the difference in their ionization potential, expressed in percentage of the potential. In agreement with the hypothesis of Goldschmidt, according to which a complete diadochy requires a close similarity in ionization potential, the difference between the ionization potentials is very small for the pairs Si⁴⁺-Ge⁴⁺, K⁺-Rb⁺, Fe²⁺-Co²⁺, Mg²⁺-Fe²⁺, and Al³⁺-Ga³⁺. The remarkably extensive diadochy in these pairs is well known. The difference between zinc and ferrous iron is smaller than the difference between zinc and magnesium. In

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fact, zinc shows a closer geochemical relationship to iron than to magnesium. The difference between sodium and univalent copper is great, and, as a matter of fact, no diadochy exists between these metals in ionic minerals.

In contradiction to Goldschmidt's rule, the difference between the ionization potentials of rubidium and univalent thallium is great. The two metals, however, occur together in rocks and show only relatively small variations in their abundance ratio in various rocks and minerals. Moreover, despite the fact that nickel has a decidedly closer geochemical relationship to magnesium than to bivalent iron, the difference between the ionization potentials of Ni^{2+} and Mg^{2+} is greater than the difference between Ni^{2+} and Fe^{2+} .

Along with the properties of the atoms and ions, their environment—viz., the atomic arrangement of the structure—evidently affects the degree of diadochy. The influence of crystal structure on diadochy is illustrated by the pair aluminum–ferric iron. It is well known that in many minerals aluminum is partly replaced by trivalent iron, and vice versa, particularly in minerals in which aluminum is 6-co-ordinated, e.g., in garnets and in spinels. Most of the common rock-making mineral groups which carry octahedrally co-ordinated aluminum (pyroxenes, amphiboles, micas, etc.) afford additional examples of this kind of diadochy. Ferric iron has a remarkable reluctance to occur in a tetrahedral co-ordination. In some instances, however, it occurs inside an oxygen tetrahedron (ferriiferous orthoclase, cronstedtite; see chap. 33). On the other hand, some common aluminum minerals are known in which the octahedrally co-ordinated aluminum apparently cannot become replaced by ferric iron. The most striking examples of such minerals are the three simple aluminum silicates, andalusite, kyanite, and sillimanite, which are very poor in, or entirely devoid of, ferric iron. It is possible that the lack of diadochy between aluminum and ferric iron in the three minerals depends on the manner in which the neighboring $[\text{AlO}_6]$ groups are linked together in the structure. In the three minerals the neighboring $[\text{AlO}_6]$ groups share two oxygen atoms and consequently have a common edge.

Among other examples of the influence of the crystal structure on diadochy the following should be mentioned: With respect to potassium, rubidium is more strongly enriched in the mica than in the potash feldspar of the same rock; bivalent manganese replaces calcium in apatite but not in anorthite; with respect to zirconium, haf-

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nium appears to become more strongly enriched in thortveitite than in zircon.

The electrostatic neutrality of the structure must be maintained in diadochic substitution. Therefore, even though the similarity of electric charge of the two ions replacing each other is not necessary for the diadochy, the ionic charge affects the substitution. Two possibilities exist:

1. The charges of the two ions replacing each other are similar.
2. An ion is replaced by another ion with a different charge. The charge of the second ion may be either lower or higher than the charge of the first ion.

TABLE 5.15
COMMON EXAMPLES OF DIADOCHIC SUBSTITUTION
IN MINERALS

DIADOCHIC SUBSTITUTION WITH:		
Unchanged Charge	Increasing Charge	Decreasing Charge
Mg^{2+} - Fe^{2+} - Mn^{2+} - Co^{2+} - Ni^{2+} - Zn^{2+} Al^{3+} - Ga^{3+} - Mn^{3+} - Cr^{3+} - Fe^{3+} - V^{3+} Si^{4+} - Ge^{4+} - Ti^{4+} P^{5+} - V^{5+} - As^{5+} K^{+} - Rb^{+} - Cs^{+} - Tl^{+} Ca^{2+} - Sr^{2+} - Mn^{2+} Zr^{4+} - Hf^{4+} - Th^{4+} Sc^{3+} - Y^{3+} -trivalent lanthanides Cb^{5+} - Ta^{5+} Sr^{2+} - Eu^{2+}	K^{+} - Ba^{2+} - Sr^{2+} - Pb^{2+} K^{+} - Eu^{2+} K^{+} - La^{3+} Ca^{2+} - Y^{3+} Mg^{2+} - Sc^{3+} Mg^{2+} - Al^{3+} - Fe^{3+} - Cr^{3+} - V^{3+} Si^{4+} - P^{5+} Sc^{3+} - Zr^{4+} - Hf^{4+} Zn^{2+} - Ga^{3+} - In^{3+} Ti^{4+} - Cb^{5+} - Ta^{5+} Fe^{2+} - Sc^{3+}	O^{2-} - OH^{-} - F^{-} Si^{4+} - Al^{3+} - B^{3+} Si^{4+} - Be^{2+} Ca^{2+} - Na^{+} Mg^{2+} - Li^{+} P^{5+} - Si^{4+} W^{6+} - Cb^{5+} - Ta^{5+}

Table 5.15 gives a number of examples of diadochic substitution in minerals. A more thorough description of the examples is given in Part II.

One of the most illustrative examples of diadochy between two ions of similar charge is probably the pair Fe^{2+} - Mg^{2+} . The diadochy of these ions plays an important role in almost all ferromagnesian minerals of rocks. Ferrous iron and magnesium replace each other in all proportions. However, it is remarkable that, in some minerals for which members of different Fe^{2+} : Mg^{2+} ratios are known, either one of the pure end-members appears to be unstable in conditions prevailing during the formation of rocks. Orthoferrosilite, the pure ferrous end-member of the orthorhombic pyroxenes, and the pure magnesian end-member of the orthorhombic amphiboles (the anthophyllite series) may be mentioned as examples of such compounds. It may

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be concluded, on the basis of thermodynamic reasoning, that changes occur in the ferrous iron:magnesium ratio of different minerals in the same rock. Thus, e.g., the distribution of ferrous iron and magnesium between olivine and orthopyroxene in ultrabasic rocks consisting essentially of the two minerals appears to depend on the abundance ratio of olivine and pyroxene in the rock, on the total iron:magnesium ratio, and on the temperature range of formation of the rock.

In diadochic substitution in which the charges of the two replacing ions are not similar, the electrostatic neutrality will be disturbed and consequently must be re-established. This may be done in various ways, e.g., through simultaneous substitution of another ion in the structure. The most illustrative example is the substitution of CaAl by NaSi in the plagioclase series. It is possible that the small content of lanthanum sometimes present in potash feldspar is a result of the substitution of KSi by LaBe . Lanthanum might be present in potash feldspar as the hypothetical compound $\text{La}[\text{AlBeSi}_2\text{O}_8]$. Other examples are the substitution of FeW by ScCb in wolframite, of ZnS by GaAs in sphalerite, etc. In other instances the neutrality is re-established by introducing additional ions outside the regular framework of the structure. An example is the diadochy between calcium and yttrium in yttriofluorite. An additional fluorine ion is introduced into the yttriofluorite structure, and a statistical disorder results. The opposite manner of re-establishing electric neutrality in the structure is to leave one structural position vacant. An example is the diadochy between the groups $[\text{SiO}_4]$ and $[(\text{OH})_4]$ in hydrogarnets. In this substitution the position of the silicon atom inside the tetrahedron will be left unoccupied. Another example is the diadochy 3 Mg -2 Al in micas in which one of the positions of the Mg^{2+} ions is left vacant.

CAMOUFLAGE, CAPTURING, AND ADMISSION OF TRACE ELEMENTS

The diadochic substitution in common rock-making minerals evidently regulates the manner of occurrence of the most abundant elements of the upper lithosphere. The influence of diadochy on the geochemistry of the trace elements is still more important.

According to their manner of occurrence in igneous rocks, the trace elements may be divided into two groups. The first group consists of the trace elements which usually form independent minerals which occur in the rocks as accessory constituents. This group includes, among others, sulfur (in sulfide minerals), phosphorus (in apatite and

monazite), zirconium (in zircon), fluorine (in fluorite), the rare-earth metals (in monazite and allanite), carbon (in carbonate minerals), and titanium, in part (in ilmenite, sphene, and rutile). The elements of the second group, on the other hand, seldom, if ever, form independent minerals except in rocks in which they happen to be very strongly enriched. Typical examples of such elements are manganese, rubidium, barium, strontium, chromium, and vanadium. The average content of these elements in igneous rocks is too low to allow the formation of their independent minerals. Notwithstanding the fact that rubidium is more abundant in igneous rocks than zirconium is, no rubidium minerals are known. Chromium forms an independent mineral, viz., chromite, in ultrabasic rocks in which the content of chromium is relatively high (average content 0.34 per cent Cr). The distinction between the two groups of elements, however, is not sharp. Some elements, such as lead (frequently contained in rocks as galena) and boron (in tourmaline), are intermediate.

Vernadsky (1924), in his geochemical classification of the elements, established the group of the dispersed elements. This group includes the following elements: Li, Sc, Ga, Br, Rb, Y, In, I, Cs. According to Vernadsky, these elements will never become considerably enriched during the major cycle, and they usually form no independent minerals. They are dispersed in minerals of other more abundant elements and do not prefer the company of any particular element. However, the geochemical classification of the elements given by Vernadsky is now obsolete and in certain respects erroneous and will therefore not be described here. At any rate, his idea of a preferentially dispersed manner of occurrence of certain elements agrees with present geochemical information.

According to Goldschmidt (1937*a*, 1944*b*), three structurally different types of diadochy regulate the dispersed manner of occurrence of the trace elements.

1. *Camouflage (Tarnung)*.—A trace element replaces diadochically a common element with similar valence. Camouflage takes place when, e.g., gallium replaces aluminum in silicates, oxides, and some other minerals, and when germanium replaces silicon in silicates.

2. *Capturing (Abfangen)*.—A trace element replaces a common element with lower valence. Because of its higher charge, the ion of the trace element becomes incorporated into the structure more firmly than does the ion of the common element. The trace element is captured by the structure. Examples of capturing are the occurrence of

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scandium in magnesium minerals and of barium and lead in potassium minerals.

3. *Admission*.—A trace element replaces a common element with higher valence. Consequently, admission is energetically the opposite of capturing. Because of the lower charge of the trace element, the replacement weakens the structure. Examples of admission are the substitution of magnesium by lithium in silicates, phosphates, and some other minerals, and the replacement of oxygen by fluorine in sphene and other minerals.

Other examples of camouflage, capturing, and admission are mentioned in Table 5.15 and in Part II of this book.

CRYSTALLIZATION OF MAGMAS AND ITS PRODUCTS

COMPOSITION OF MAGMAS AND OF IGNEOUS ROCKS

IGNEOUS AND QUASI-IGNEOUS ROCKS

In the subsequent paragraphs the geochemistry of the rocks and mineral formations will be discussed which, in a broad sense of the word, may be called igneous. It appears pertinent to start with a few words to explain the meaning of the terms igneous and magmatic because in recent years much confusion has arisen on this score. According to the terminology used in this book, a rock is igneous or magmatic if the material of which it consists has been entirely molten before attaining its present structure and composition. The material of the igneous rocks is either primary juvenile (true igneous rocks) or secondary, being derived from basement rocks by remelting (quasi-igneous or pseudo-igneous rocks). Of course, it is often extremely difficult or even impossible to produce conclusive evidence as to the true igneous or quasi-igneous character of a rock. This concerns particularly the more acidic rock types, such as granites and granodiorites. As a matter of fact, many of the rocks called igneous and included in the average calculations presented in Table 2.1 may actually be quasi-igneous. However, notwithstanding the geological significance of the igneous-looking rocks formed by metasomatic infiltration and recrystallization processes (granitized rocks, etc.), the phenomena connected with the crystallization of a rock melt are geochemically important and must be separately discussed. This concerns particularly the laws which govern chemical differentiation caused by the incorporation of a number of elements in the structures of the crystallizing minerals.

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AVERAGE MINERALOGICAL COMPOSITION OF IGNEOUS ROCKS

In chapter 2 the average chemical composition of igneous rocks was used to illustrate the average composition of the Sial crust. However, the composition of a single igneous rock very seldom even approaches the average composition as presented in Table 2.1. The upper lithosphere, which may originally have been rather homogeneous chemically, has differentiated, and at least a part of the numerous types of igneous rocks have been formed thereby.

According to Goldschmidt (1933*a*), opdalite, an igneous rock found at the Opdal-Indset in southern Norway, approaches in composition the average of igneous rocks. Opdalite consists mainly of plagioclase, potash feldspar, hypersthene, quartz, and augite. The chemical composition of opdalite is presented in Table 2.1, as is the composition of the average igneous rock calculated by Clarke and Washington (1924) and by Vogt (1931). The close chemical relationship between opdalite and the average igneous rock is readily established by comparing the three analyses.

The comparison between the average chemical composition of igneous rocks and the composition of the various classes of calc-alkalic igneous rocks presented in Table 5.32 shows that the igneous rocks, on an average, correspond to diorites or granodiorites. However, in the average composition the content of the alkali metals, particularly of potassium, is somewhat higher than in diorites and granodiorites.

The average chemical composition of igneous rocks may be used as a starting point in the survey dealing with the manner of occurrence of the elements therein. It must be noted that the average chemical composition of the igneous rocks indicates only the abundance of the elements and not their manner of occurrence as characterized by the minerals in which the elements are incorporated. The average mineralogical composition of igneous rocks is, therefore, of fundamental importance for geochemical consideration of the occurrence of the elements in such rocks. The average mineralogical composition of the igneous rocks is summarized in Table 5.16, which contains the norms computed for the average composition of igneous rocks given by Vogt (1931) and by Clarke and Washington (1924). The normative composition is presented, in order to allow comparison with the mode of the average igneous rock reported by Clarke (1924). His values

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represent the average mode or actual mineralogical composition of about 700 igneous rocks.

Geochemically, it is of importance to consider the abundance of minerals and mineral groups in igneous rocks. Table 5.16 shows that the feldspars form nearly 60 per cent of the mass of igneous rocks and that therefore the feldspars are geochemically the most important group of minerals. The pyroxenes and amphiboles come next. They are essentially silicates of iron and magnesium and consequently include the bulk of the two metals present in the upper lithosphere.

TABLE 5.16
AVERAGE MINERALOGICAL COMPOSITION OF IGNEOUS ROCKS
(Composition Given in Per Cent by Weight)

CONSTITUENT	NORM CALCULATED FROM AVERAGE COMPOSITION OF IGNEOUS ROCKS GIVEN BY—		MINERAL	MODE AC- CORDING TO CLARKE
	Vogt	Clarke and Washington		
Orthoclase.....	21 6	18 8	Feldspars	59.5
Albite.....	29 2	33 0	Quartz	12.0
Anorthite.....	16 2	15.7	Hornblende and pyroxene	16 8
Quartz.....	17 6	9 0	Biotite.....	3 8
CaSiO ₃	2 0	3 3	Titanium minerals . .	1 5
MgSiO ₃	6 1	8 8	Apatite	0 6
FeSiO ₃	3 7	5 4	Other rock-making miner- als	5 8
MnSiO ₃		0 2		
Ilmenite.....	1 0	2 0		
Hematite.....	2 2	3 1		
Apatite.....	0.4	0.7		
Total.....	100.0	100.0	Total...	100 0

Quartz occupies the third place, but all other minerals are, both quantitatively and geochemically, of minor importance.

THE MOST IMPORTANT ROCK-MAKING MINERALS OF IGNEOUS ROCKS

During the crystallization of a calc-alkalic magma, three different stages are usually distinguished, viz., the early magmatic stage, the main stage of crystallization, and the late magmatic stage. The crystallization of magmas will be discussed in later paragraphs of this chapter. Among the products of crystallization, the igneous rocks formed during the main stage predominate in the upper lithosphere. They are principally composed of the eight main elements of the upper lithosphere, viz., oxygen, silicon, aluminum, iron, calcium,

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sodium, potassium, and magnesium. In silicate minerals, sodium, potassium, and calcium are found to be predominantly combined with aluminum and oxygen to form aluminosilicates, whereas iron and magnesium do not possess this property. The feldspars and feldspathoids, which are the most typical aluminosilicates, are, together with quartz, the chief silicic rock-making minerals. Their most typical cations are Na^+ , K^+ , Ca^{2+} , and Al^{3+} . The fenic constituents of igneous rocks contain Mg^{2+} , Fe^{2+} , Fe^{3+} , and, in part, Ca^{2+} and Al^{3+} .

Only those mineral groups and species will be treated in this book which, according to Table 5.16, are very abundant or which are significant in certain rare, but geochemically important, rocks. Consequently, a number of mineralogically and petrologically important rare minerals which may characterize certain igneous rocks will not be considered in this chapter, the reason being their geochemical insignificance. Only the following groups and species will be discussed:

Feldspars	Olivines
Feldspathoids	Quartz
Pyroxenes and amphiboles	Micas

However, it is important to notice that numerous accessory minerals which usually occur in igneous rocks in very small quantities may be geochemically more significant than certain species found as main constituents in rare rock types. It is evident, for example, that apatite, zircon, sphene, and the ore minerals are more common and more abundant constituents of igneous rocks than are many of the chief rock-making constituents of rare rocks, such as nepheline and leucite in alkalic rocks. The most important accessory minerals of igneous rocks are also of geochemical importance and consequently will be incorporated into the discussion.

FELDSPARS

STRUCTURE OF THE FELDSPARS

Notwithstanding the fact that the feldspars are both petrologically and geochemically the most important mineral group of the upper lithosphere, they are mineralogically rather incompletely known. Even though optical methods have been developed for the chemical characterization of the feldspars (see, e.g., Wenk, 1945), the petrologically important relationship between optical properties and chemical composition in natural feldspars is far from being definitely solved. Numerous examples show that conclusions concerning the

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chemical composition of the feldspars drawn from their optical properties are not always unequivocal. Moreover, the optical properties of the feldspars appear to depend, in a curious way, on the antecedents of the material. This is probably also the case with the frequent twinning of the feldspars (Köhler, 1948).

The variation of optical and other properties is understood on the basis of crystal structure. Even though a detailed knowledge of the crystal structure of the feldspars still must await the results of future investigations, some fundamental features are well understood. All feldspars possess a continuous three-dimensional silicon-oxygen-aluminum network in which $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra share all

TABLE 5.17
THE NATURAL FELDSPARS

Group	Symbol	Mineral	Crystal system	Formula
Barium feldspar	Cn	Celsian Hyalophane	Monoclinic Monoclinic	$\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ $\text{Cn} + \text{Or}$
Potash feldspar	Or {	Orthoclase Adularia Microcline	Monoclinic Monoclinic Triclinic	} $\text{K}[\text{AlSi}_3\text{O}_8]$
Potash-soda feldspar . . .		Sanidine Soda orthoclase Anorthoclase	Monoclinic Monoclinic Triclinic	} $\text{Or} + \text{Ab}$
Plagioclase	Ab An	Albite Anorthite	Triclinic Triclinic	$\text{Na}[\text{AlSi}_3\text{O}_8]$ $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$

four oxygen atoms with the neighboring tetrahedra. The resulting framework is flexible (Taylor, 1934) and gives rise to overstructures and other complications which greatly handicap a detailed study.

For the reasons explained above, the division of the feldspar minerals is still somewhat uncertain in details. If, along with a given chemical composition, a definite crystal structure with exactly fixed positions of the atoms and ions is accepted as a requirement for distinguishing between mineral species, the classification of the feldspars becomes difficult. The flexibility of the silicon-oxygen-aluminum framework makes the whole conception of a feldspar species more or less hazy. This circumstance appears to be characteristic of some alkali feldspars. Therefore, the customary classification of natural feldspars, presented in Table 5.17, must be considered to be only tentative.

The fundamental unit of the feldspar structure, the $[\text{SiO}_4]$ or $[\text{AlO}_4]$

tetrahedron, shares all four oxygen ions with the neighboring tetrahedra. In all feldspars, four tetrahedra are linked together to a four-ring, which apparently is a very stable unit. When viewed in the direction of the crystallographic a -axis, the framework consists of tetrahedra arranged in tetragons and collapsed octagons (see Fig. 5.3). The Na^+ , K^+ , Ca^{2+} , and Ba^{2+} ions are situated in the octagonal openings. Because the four-rings are relatively strong, the cleavage planes parallel to (001) and (010) break the bonds between the four-rings and leave the rings themselves unaffected (Taylor, 1933; Taylor, Darbyshire, and Strunz, 1934).

The crystal symmetry of the feldspars appears to depend on the cations. The feldspars are either monoclinic (pseudo-monoclinic) or triclinic. If the cations situated inside the collapsed octagonal chains

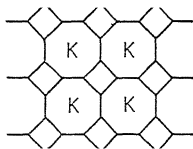


FIG. 5.3.—Structure of the feldspars. The markedly pseudo-tetragonal a -axis is perpendicular to the plane of the paper. K marks the places of the K^+ ions.

are relatively small (Na^+ , Ca^{2+}), a true triclinic symmetry results; but, if the cations are large (K^+ , Ba^{2+}), the symmetry is strictly monoclinic or almost monoclinic (pseudo-monoclinic). The flexibility of the silicon-oxygen-aluminum framework makes a variation in the co-ordination number of the cations with reference to oxygen possible, with but slight changes in the framework itself. In the albite structure, Na^+ is 6-co-ordinated, whereas Ca^{2+} in the anorthite structure is 7-co-ordinated. The co-ordination number of K^+ and Ba^{2+} is 9. The rather irregular configuration of the oxygen ions around the potassium and barium ions is due to the great size of these cations.

The fact that each oxygen atom is shared by two neighboring $[\text{SiO}_4]$ or $[\text{AlO}_4]$ tetrahedra is a special feature of all three-dimensionally continuous framework structures. Formally, they may be derived from silica, in which the $\text{Si}:\text{O}$ ratio is 1:2. If, in a unit containing 12 molecules of silica ($\text{Si}_{12}\text{O}_{24}$), 3 Si^{4+} ions are replaced by Al^{3+} ions, 3 univalent positive ions must be introduced into the empty spaces of the framework to maintain the electric neutrality of the structure. Albite represents the result of the replacement (Table 5.18).

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If, in the same silica unit, 4 Si^{4+} ions are replaced by Al^{3+} ions, 4 univalent cations must be introduced, and the result is a compound like soda leucite. If 6 Si^{4+} ions are replaced by Al^{3+} ions, the electrostatic neutrality can be maintained by introducing either 6 univalent cations to form nepheline or 3 bivalent cations, by which anorthite is produced. The Al:Si ratio indicates the degree of silicification of the structure.

In the feldspar structure, all aluminum is 4-co-ordinated inside the $[\text{AlO}_4]$ tetrahedra. In some other minerals like pyroxenes, amphiboles, and the simple aluminum silicates (sillimanite, andalusite), the co-ordination number of aluminum is only partly 4, and partly 5 (in

TABLE 5.18
FORMAL DERIVATION OF ALUMINOSILICATES FROM SILICA

Silica	Replacement	Result	Al:Si
$\text{Si}_{12}\text{O}_{24}$	3 Si by 3(NaAl)	3 $\text{NaAlSi}_3\text{O}_8$ Albite	1:3
$\text{Si}_{12}\text{O}_{24}$	4 Si by 4(NaAl)	4 $\text{NaAlSi}_2\text{O}_6$ Soda leucite	1:2
$\text{Si}_{12}\text{O}_{24}$	6 Si by 6(NaAl)	6 NaAlSiO_4 Nepheline	1:1
$\text{Si}_{12}\text{O}_{24}$	6 Si by 3(CaAl_2)	3 $\text{CaAl}_2\text{Si}_2\text{O}_8$ Anorthite	1:1

andalusite) or 6 (in sillimanite). The frequent occurrence of both 4- and 6-co-ordinated aluminum in silicate minerals of the upper lithosphere (see under "Crystal Chemistry and Geochemistry," p. 116) makes it convenient to apply different designations to the two types of aluminum-bearing silicate minerals. According to the terminology customarily employed by some silicate chemists (e.g., Eitel, 1941), the silicates containing 4-co-ordinated aluminum in similar structural positions as the silicon ions are called aluminosilicates. Silicates in which aluminum does not replace silicon but occurs outside the complex silicon-oxygen network are called aluminum silicates. The feldspars are typical aluminosilicates; probably the best example of an aluminum silicate is kyanite, in which all aluminum is 6-co-ordinated. Of course, many important minerals and mineral groups represent intermediate types in which aluminum occurs both in 4- and in 6-co-ordination.

The formation of silicates with a continuous three-dimensional

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framework of $[\text{SiO}_4]$ tetrahedra requires the replacement of silicon by another cation with a lower charge. In the aluminosilicates, silicon is replaced by aluminum, and the electric neutrality of the structure is maintained by the introduction of new cations. However, silicon may be replaced also by the small Be^{2+} and B^{3+} ions. Beryllium is always 4-co-ordinated in silicate minerals; the co-ordination number of boron is either 3 or 4. Silicates containing $[\text{BeO}_4]$ or $[\text{BO}_4]$ groups in the continuous three-dimensional framework of tetrahedra are called beryllosilicates and borosilicates, respectively. Formally, they may be derived from silica in the same way as are the aluminosilicates. Examples of the borosilicate and beryllosilicate minerals are danburite, $\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$, and probably gadolinite, $\text{Y}_2\text{Fe}[\text{O}|\text{BeSiO}_4]_2$.

THE FELDSPAR MINERALS AND THEIR CHEMICAL COMPOSITION

THE PLAGIOCLASE SERIES.—In petrological nomenclature it is customary to designate mixtures with different Ab:An ratios as follows:

Name	An Molecular Per Cent
Albite.....	0- 10
Oligoclase.....	10- 30
Andesine.....	30- 50
Labradorite.....	50- 70
Bytownite.....	70- 90
Anorthite.....	90-100

The average chemical composition of plagioclase of some igneous rock classes is presented in Table 5.19. All figures in this table are from Chirvinsky (1931). In the lower part of the table the molecular composition is computed, given as the percentage of the An, Ab, and Or molecules. The values show that the series of natural plagioclases is no strict two-component system but almost always contains small amounts of potash feldspar in solid solution. The potash content (Or) appears to be fairly uniform and, to a first approximation, independent of the Ab:An ratio. The Ab:An ratio is different in different groups of igneous rocks.

The albite-anorthite series is usually regarded as one of the most ideal isomorphous series among the silicate minerals. The occurrence of all intermediate solid solutions between pure albite and pure anorthite in rocks, the smooth and continuous liquidus and solidus curves in the phase diagram of the plagioclases (Bowen, 1913), along with other features, appear to indicate that the isomorphism between albite and anorthite is perfect. According to Chao and Taylor (1940), however, some features in the X-ray data indicate that the isomor-

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phic relationship between albite and anorthite is not too simple. These authors state that albite and anorthite have slightly different structures. The dimensions of the unit cells of the two minerals are fairly similar, except that the length of the *c*-axis of anorthite is twice the length of the *c*-axis of albite. Three different structures exist in the albite-anorthite series: albite structure extends from pure albite to >22 An, an intermediate structure occupies the range from <57 An to >67 An, and anorthite structure starts with <80 An. The pla-

TABLE 5.19

AVERAGE COMPOSITION OF FELDSPARS OF VARIOUS IGNEOUS ROCKS
(Composition as Oxides Given in Weight Percentage, as Feldspar
Molecules in Molecular Percentage)

CONSTITUENT	POTASH FELDSPAR, GRANITES AND GRAN- ITE SYE- NITES	ANOR- THOCLASE, VOLCANIC ROCKS	PLAGIOCLASE				
			Gabbros and Nor- ites	Diorites	Granites and Gran- ite Peg- matites	Nepheline Syenites	Syenites
No. of analyses...	18	30	69	26	59	11	4
SiO ₂	64.13	65.61	52.47	55.11	64.60	64.95	63.51
Al ₂ O ₃	19.40	20.42	29.31	27.52	21.46	21.33	22.56
CaO	1.00	1.45	11.82	9.39	2.51	1.72	4.20
Na ₂ O	2.68	7.91	4.12	5.02	9.22	9.64	8.02
K ₂ O	11.71	3.82	1.47	1.33	1.12	1.51	0.95
Total . . .	98.92	99.21	99.19	98.37	98.91	99.15	99.24
An	5	7	58	47	13	8	21
Ab	25	70	34	45	81	83	74
Or	70	23	8	8	6	9	5
Total	100	100	100	100	100	100	100

gioclases of intermediate composition consist of sheets along the direction of the *c*-axis. The sheets have alternating albite and anorthite structure and their thickness is only a few unit cells.

According to the considerations on the structural order and disorder of isomorphous mixtures presented by Buerger (1948), at elevated temperatures albite and anorthite undoubtedly form solid solutions with all Ab:An ratios. However, at room temperature a double isomorphism exists. An unmixing takes place in plagioclases of intermediate composition in a temperature region well below the solidus curve of the phase diagram. This hypothesis requires further experimental verification.

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THE BARIUM FELDSPARS.—Celsian and hyalophane are extremely rare, and therefore their geochemical significance is small. The isomorphism between celsian and orthoclase (or adularia) is believed to be continuous, but this hypothesis thus far has not been verified by structural investigations. Mineralogically, the barium feldspar series is analogous to the plagioclase series.

THE POTASH FELDSPARS.—The structural relationships among the three potash feldspars—orthoclase, adularia, and microcline—have thus far not been studied in detail. The structure of orthoclase is accurately known (Chao, Hargreaves, and Taylor, 1939). In orthoclase some of the bonds between O^{2-} and K^{+} ions appear to be dead. The existence of dead bonds is structurally important; they may be frequent in silicate structures in which electrostatic neutrality is not completely maintained.

In contrast to the suggestion of E. Mallard in 1876 that orthoclase is submicroscopically twinned microcline, it is now generally held that the difference between the two minerals is based on a real difference in atomic arrangement.

The average chemical composition of potash feldspar from granites and granite syenites is presented in Table 5.19. The analyses indicate that the common potash feldspars of acidic igneous rocks contain appreciable amounts of the sodic component.

THE POTASH-SODA FELDSPARS.—A potash feldspar approaching the composition $KAlSi_3O_8$ is a great rarity in Nature. Orthoclase, microcline, and even adularia almost always contain considerable quantities of soda feldspar. No exact terminology, corresponding to that of the plagioclases, has ever been suggested for the intermediate members in the Or-Ab series. Orthoclase and microcline with a relatively high soda content are simply called soda orthoclase and soda microcline, respectively. The molecules $KAlSi_3O_8$ and $NaAlSi_3O_8$ probably form a continuous series of solid solutions at high temperatures, but below the temperature range of the solidus curve there is a gap in the isomorphic series, and it expands in width toward lower temperatures. Anorthoclase is the pseudo-monoclinic equivalent of an albite-rich plagioclase with a high potash content. The average chemical composition of anorthoclase from volcanic rocks is presented in Table 5.19.

The implication of the name sanidine is not chemical but structural. It refers to a potash feldspar, usually rich in the soda component and with optical properties deviating from those of orthoclase

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and adularia. The structural difference between orthoclase and sanidine is not definitely established. However, it appears evident that sanidine represents a high-temperature form of potash feldspar or of potash-soda feldspar in which the potassium and sodium ions are distributed at random (Spencer, 1930, 1937, 1938). On prolonged heating at temperatures not far below their melting point, the potash-soda feldspars become permanently sanidinized.

It was realized long ago that orthoclase perthite and microcline perthite are regular intergrowths of potash-rich and soda-rich components. Recent investigations by Chao, Smare, and Taylor (1939) and by Chao and Taylor (1940) have shed more light on the perthite problem. The perthitic unmixing, by diffusion of the alkali metal ions through the relatively open feldspar structure, results in the formation of an ordinary orthoclase or microcline component and of a sodic component different from albite.

The existence of a monoclinic soda feldspar, called barbierite, was suggested by Schaller (1910), and a similar suggestion was made by Ito (1938) on the basis of structural investigations. The supposed monoclinic soda feldspar mostly occurs in sanidine as a product of unmixing. Further verification is obviously needed (Chao and Taylor, 1940).

CATIONS ACCOMMODATED IN THE FELDSPAR STRUCTURE

The list of feldspar minerals presented in Table 5.17 raises the question whether sodium, calcium, potassium, and barium are the only metals able to form a stable aluminosilicate with feldspar structure. The cations of these metals are relatively large and consequently are able to fill the empty spaces in the octagonal chains of the feldspar structure. It is remarkable that such metals as magnesium and iron do not enter into the feldspar structure. The reason apparently is the small size of the Fe^{2+} and Mg^{2+} ions; they require a 6-fold co-ordination.

Schiebold (1931) has discussed the stability of aluminosilicates of the feldspar type. On the basis of the Born-Haber cycle, Schiebold estimated the heat of formation of the feldspar compound and the heat of formation of the component oxide mixture for a number of univalent and bivalent metals. The heat of formation of the hypothetical feldspars, calculated from Schiebold's figures, is presented in Table 5.20. It must be kept in mind that, because of the scarcity of reliable data underlying the computations, the values given in Table 5.20 are to be considered only rough approximations.

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The values listed in this table agree qualitatively with general mineralogical and geochemical observations. The values of ΔH are negative for the feldspar compounds of sodium, potassium, rubidium, cesium, thallium, calcium, strontium, barium, and lead, whereas the ΔH values for the feldspar compounds of the other metals listed in Table 5.20 are positive. The metals for which the ΔH values are negative most probably form a stable feldspar structure, whereas

TABLE 5.20

APPROXIMATE HEAT OF FORMATION FROM COMPONENT OXIDES (ΔH) OF HYPOTHETICAL FELDSPARS OF SOME UNIVALENT AND DIVALENT METALS

Feldspar Compound	Heat of Formation (ΔH) (kcal/mol)
LiAlSi ₃ O ₈	+ 35
NaAlSi ₃ O ₈	- 59
KAlSi ₃ O ₈	-117
RbAlSi ₃ O ₈	-130
CsAlSi ₃ O ₈	-145
CuAlSi ₃ O ₈	+ 91
AgAlSi ₃ O ₈	+126
AuAlSi ₃ O ₈	+134 (?)
TlAlSi ₃ O ₈	- 46
BeAl ₂ Si ₂ O ₈	+214
MgAl ₂ Si ₂ O ₈	+ 62
CaAl ₂ Si ₂ O ₈	- 61
SrAl ₂ Si ₂ O ₈	- 92
BaAl ₂ Si ₂ O ₈	-133
ZnAl ₂ Si ₂ O ₈	+100
CdAl ₂ Si ₂ O ₈	+ 41
HgAl ₂ Si ₂ O ₈	~+ 67
MnAl ₂ Si ₂ O ₈	+ 42
FeAl ₂ Si ₂ O ₈	+ 44
CoAl ₂ Si ₂ O ₈	+ 92
NiAl ₂ Si ₂ O ₈	+109
PbAl ₂ Si ₂ O ₈	- 34

those for which ΔH is positive do not. As a matter of fact, sodium, potassium, calcium, and barium feldspars exist in Nature. A stable strontium feldspar was prepared by Eskola (1922), and a stable lead feldspar by Köhler (1935). Rubidium is found as a frequent constituent of potash feldspars, and cesium and thallium are also reported to occur in potash feldspars, particularly in those from pegmatites. On the other hand, lithium feldspar appears from Table 5.20 to be unstable; in fact, it has never been found in Nature. Even in lithium pegmatites, in which it is highly concentrated, lithium forms spodumene, petalite, and other independent minerals. The fact that small

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amounts of lithium may be present in pegmatite feldspars affords an example of a structure (feldspar) containing in solid solution small quantities of a compound ($\text{LiAlSi}_3\text{O}_8$) which is not stable alone.

A ferriferous orthoclase with up to 11–12 molecular per cent KFeSi_3O_8 has been found in Madagascar (Lacroix, 1922). Confirming the early synthesis of P. Hautefeuille and A. Perrey, Faust (1936) definitely established the existence of the pure ferriferous analogue of potash feldspar, in which ferric iron replaces aluminum. Potash feldspar analyses reported in literature sometimes show traces of Fe_2O_3 . This fact appears to indicate that the ordinary potash feldspar may contain small quantities of the ferriferous compound in solid solution. It is very probable that the red color, characteristic of many potash feldspars, has originated through unmixing and subsequent disintegration of the ferriferous component under the formation of hematite.

FELDSPATHOIDS

The content of the feldspathoids is not given separately in the average mineralogical composition of igneous rocks, as indicated in Table 5.16. The reason is that the alkali-rich rocks in which these minerals occur are very rare. Even though the feldspathoids in the alkalic rocks are geochemically as important as the feldspars in calc-alkalic rocks, their geochemical role in the upper lithosphere is rather unimportant. However, with reference to their structure and composition, the feldspathoids are comparable to the feldspars.

The concept of the feldspathoids is merely petrographic. The individual minerals classified among the feldspathoids form no separate mineral group which would correspond to the feldspar group. The following minerals are usually included among the feldspathoids:

Nepheline,	$\text{Na}[\text{AlSiO}_4]$
Kaliophilite,	$\text{K}[\text{AlSiO}_4]$
Kalsilite,	$\text{K}[\text{AlSiO}_4]$
Leucite,	$\beta\text{-K}[\text{AlSi}_2\text{O}_6]$
Cancrinite,	$(\text{Na}_2, \text{Ca})_4[\text{CO}_3] (\text{H}_2\text{O})_{0-3} (\text{AlSiO}_4)_6]$
Sodalite,	$\text{Na}_8[\text{Cl}_2] (\text{AlSiO}_4)_6]$
Noselite,	$\text{Na}_8[\text{SO}_4] (\text{AlSiO}_4)_6]$
Hauynite,	$(\text{Na}, \text{Ca})_{8-4}[(\text{SO}_4)_{2-1} (\text{AlSiO}_4)_6]$

Like the feldspars, these minerals have a continuous three-dimensional framework of $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra. Along with the large cations Na^+ , K^+ , and Ca^{2+} , the anions Cl^- , SO_4^{2-} , and CO_3^{2-} in some of the feldspathoids populate the interstitial spaces of the complex silicon-oxygen-aluminum framework. In most feldspathoids the

Al:Si ratio is 1:1; only in leucite is it 1:2. In potash and soda feldspars the ratio is 1:3, and in lime feldspar 1:1. Because pure anorthite is extremely rare in Nature, the actual Al:Si ratio in the plagioclases lies between 1:1 and 1:3. Consequently, the Al:Si ratio in the chemically corresponding feldspars and feldspathoids is different in so far as the number of aluminum atoms is greater in the feldspathoids in relation to the number of silicon atoms. In other words, the degree of silicification is higher in the feldspars than in the feldspathoids. The lattice energy of the feldspathoids is probably lower than the lattice energy of the corresponding feldspars.

Owing to their relative rarity, cancrinite, sodalite, noselite, and hauynite are of minor importance in the geochemistry of the upper lithosphere. Kaliophilite (phacellite) and kalsilite have been found only at Vesuvius and in Uganda, respectively (Bannister, 1931, 1942). Nepheline, kaliophilite, and kalsilite are all hexagonal and optically negative. It is impossible to distinguish microscopically between kalsilite and nepheline. Kaliophilite has slightly lower refractive indices than has nepheline, but apparently the difference is too small for proper identification. It seems to be possible that kaliophilite and kalsilite actually are more frequent minerals than is commonly assumed. However, their abundance compared with the abundance of nepheline is certainly low.

The compound NaAlSiO_4 is dimorphic. Nepheline, which is the low-temperature (β -) form, is stable below about $1,248^\circ \text{C.}$, whereas the high-temperature (α -) form, carnegieite, is stable above that temperature. Carnegieite has not been found in Nature. The average chemical composition of nepheline from nepheline syenites is presented, according to Chirvinsky (1931), in Table 5.21. The analysis indicates that nepheline contains appreciable amounts of potassium. Bowen and Ellestad (1937) showed that the soda:potash ratio in nepheline depends on the soda:potash ratio of the rock as a whole, in so far as nephelines from rocks richer in potash are higher in the potash component.

Nepheline also contains a little calcium, which is due to the limited isomorphism between nepheline and anorthite. However, according to Schiebold (1931), it is probable that the electric charge of the Ca^{2+} ions in the nepheline structure is not completely neutralized, and therefore the compound $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ cannot form a stable structure similar to the nepheline structure. The calcium nepheline, $\text{Ca}[\text{AlSiO}_4]_2$, which has the same bulk composition as anorthite,

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$\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$, is unknown in Nature and has never been prepared in the laboratory.

Figure 5.3 shows that the complex -Si-O-Al-network of the feldspars consists of alternating tetragonal and octagonal rings. The big cations situated outside the network populate the octagonal cavities. In nepheline the -Si-O-Al-network forms hexagonal cells in a honeycomb-like arrangement, which is shown in Figure 5.4. The structure of nepheline may be derived from the structure of tridymite. Compared with the feldspar structure, that of nepheline is less stable. Consequently, nepheline forms only when the amount of silica available is insufficient for the formation of the feldspars.

TABLE 5.21
AVERAGE CHEMICAL COMPOSITION OF
NEPHELINE AND LEUCITE
(Composition Given in Per Cent by Weight)

Constituent	Nepheline from Nepheline Syenites	Leucite from Vesuvius, Italy
No. of analyses.....	16	14
SiO_2	43 97	56.39
Al_2O_3	32 89	23 10
CaO	0 43	0 27
Na_2O	15 73	2 17
K_2O	5 45	18 05
Total...	98 47	99.98

Kaliophilite has a large and rather complicated unit cell with 54 molecules of KAlSiO_4 . It is not isomorphic with nepheline, which has only 8 molecules of NaAlSiO_4 in its unit cell. A complete series of solid solutions exists between nepheline and kalsilite. The length of the *a*-axis of the unit cell of nepheline is approximately twice that of kalsilite, and the length of the *c*-axis of the two minerals is rather similar. According to Bannister (1942), the series between nepheline and kalsilite probably is analogous to the plagioclase series. At high temperatures the isomorphism is complete, but, in lower-temperature ranges, unmixing of the end-components takes place in mixtures of intermediate composition. This hypothesis, however, needs verification.

Besides nepheline, leucite is the most abundant among the feldspathoids. The average chemical composition of leucite from the lavas

of Vesuvius is presented in Table 5.21 according to Chirvinsky (1931). The table also shows that leucite contains the corresponding soda component in solid solution. A little calcium is also present. Like $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 is also dimorphic. The orthorhombic low-temperature form of leucite is stable below 603°C ., whereas the isometric high-temperature form is stable above that temperature.

The structures of leucite and nepheline are somewhat less stable than those of potash feldspar and soda feldspar, respectively. Nepheline is unstable in association with silica and reacts therewith under the formation of albite. At temperatures below the incongruent melting point of orthoclase ($1,170^\circ\text{C}$.), leucite is also unstable in the presence of silica. Nepheline and leucite differ from each other with ref-

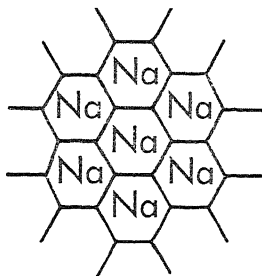


FIG. 54.—Structure of nepheline. The c -axis is perpendicular to the plane of the paper. The positions of the Na^+ ions within the hexagonal cavities are marked.

erence to their manner of occurrence. Unlike nepheline, leucite occurs in volcanic rocks which were crystallized at low pressures. In deep-seated igneous rocks potash feldspar forms instead of leucite. It is unknown whether kaliophilite and kalsilite occur in deep-seated igneous rocks.

PYROXENES AND AMPHIBOLES

STRUCTURE OF PYROXENES AND AMPHIBOLES

According to Table 5.16, the pyroxenes and the amphiboles predominate among the dark constituents of igneous rocks. Structurally, pyroxenes and amphiboles are closely related. They belong to the inosilicates, which consist of infinite chains and double chains of $[\text{SiO}_4]$ tetrahedra. In the pyroxenes the chain consists of tetrahedra, each of which shares two oxygen ions with its neighbors. In the amphiboles two infinite chains of tetrahedra are linked together by oxygen ions, and the tetrahedra share alternately two and three oxygen ions. The chains of the pyroxenes and the double chains of the

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amphiboles are arranged parallel to the *c*-axis of the crystal, and their planes are perpendicular to (010). This structure, which is presented, after Bragg (1937), in Figure 5.5, explains the difference in the cleavage of the pyroxenes and of the amphiboles. The chains and double chains are linked by various cations, and the bond between the oxygen ions and the cations is weaker than the bond between the silicon and the oxygen ions. Cleavage takes place diagonally through the

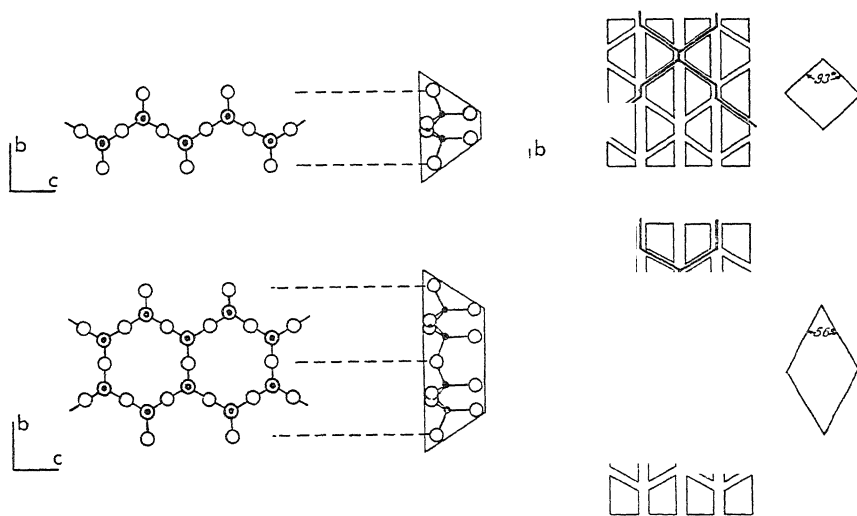
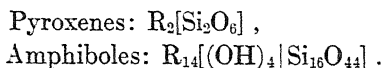


FIG. 5.5.—Structure of the silicon-oxygen chains and cleavage in the pyroxenes (*top*) and in the amphiboles (*bottom*). (Based on material from *Atomic Structure of Minerals*, by W. L. Bragg, 1937. Courtesy of Cornell University Press.)

crystal and does not break the Si-O chains. The cleavage planes are therefore parallel to (110) both in pyroxenes and in amphiboles.

GENERAL CHEMICAL COMPOSITION OF PYROXENES AND AMPHIBOLES

The pyroxene and amphibole groups contain numerous minerals which differ both mineralogically and chemically from one another. However, the following general formulas may be given for the two groups:



In these formulas, R is Mg^{2+} , Fe^{2+} , or Ca^{2+} and, in many types, Al^{3+} , Fe^{3+} , Ti^{3+} , Mn^{3+} , Mn^{2+} , Na^+ , K^+ , Li^+ , etc. In the amphiboles the OH^- group is partly replaced by O^{2-} or by F^- .

PYROXENES

Three series of pyroxenes occur in igneous rocks, as follows:

1. Orthorhombic pyroxenes or orthopyroxenes
 - Enstatite, $\text{Mg}_2[\text{Si}_2\text{O}_6]$
 - Hypersthene, $(\text{Mg}, \text{Fe})_2[\text{Si}_2\text{O}_6]$
2. Diopside-jadeite series
 - Clinoenstatite, $\text{Mg}_2[\text{Si}_2\text{O}_6]$
 - Clinoferrosilite, $\text{Fe}_2[\text{Si}_2\text{O}_6]$
 - Diopside, $\text{CaMg}[\text{Si}_2\text{O}_6]$
 - Hedenbergite, $\text{CaFe}[\text{Si}_2\text{O}_6]$
 - Johannsenite, $\text{CaMn}[\text{Si}_2\text{O}_6]$
 - Spodumene, $\text{LiAl}[\text{Si}_2\text{O}_6]$
 - Jadeite, $\text{NaAl}[\text{Si}_2\text{O}_6]$
 - Aegirite, $\text{NaFe}[\text{Si}_2\text{O}_6]$
3. Augite series
 - Augite, $\text{Ca}_{6.5}\text{Na}_{0.5}\text{Fe}^{2+}\text{Mg}_6(\text{Al}, \text{Fe}^{3+}, \text{Ti})_2[\text{Al}_2\text{Si}_{14}\text{O}_{48}]$
 - Diallage, and others

The formulas presented above are idealized. A more or less complete isomorphism exists between the various components in the three series, and the pyroxenes found in Nature are always mixtures. The pyroxenes of volcanic rocks usually are more variable in composition than are the pyroxenes of plutonic rocks. The reason is that at elevated temperatures the expanding structures allow a higher degree of diadochic substitution than at low temperatures. In the relatively rapidly solidified volcanic rocks the unmixing in the mineral structures has been limited, whereas in the deep-seated rocks the degree of the diadochic substitution has been constantly adjusted according to the decreasing temperature during crystallization.

The role of aluminum in the pyroxene structure is remarkable. In the orthorhombic pyroxenes and in those of the diopside-jadeite series, Al^{3+} is hardly, if at all, capable of substituting for Si^{4+} in the $[\text{SiO}_4]$ tetrahedra. In the augite series, however, up to one-fourth of the Si^{4+} ions may become replaced by Al^{3+} , and consequently the maximum Al:Si ratio is 1:3. Another part of aluminum occurs outside the silica network in 6-co-ordination.

The average chemical composition of some pyroxenes from igneous rocks is presented, according to Chirvinsky (1931), in Table 5.22.

The orthorhombic enstatite and hypersthene and the monoclinic clinoenstatite and clinoferrosilite are the pyroxenes with the simplest chemical composition. They contain no calcium. Chemically, hypersthene and clinoferrosilite differ from each other with reference to magnesium content. Clinoferrosilite is a pure iron silicate, whereas hypersthene always contains magnesium. Sometimes the atomic

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magnesium content in hypersthene exceeds the atomic iron content. The monoclinic clinohypersthene, which corresponds to hypersthene in composition, is a constituent of the meteorites but never occurs in terrestrial igneous rocks (see chap. 1). The structural difference between the orthorhombic and the monoclinic hypersthene is schematically presented in Figure 5.6.

TABLE 5.22
AVERAGE CHEMICAL COMPOSITION (IN PER CENT BY WEIGHT)
OF PYROXENES FROM SOME IGNEOUS ROCKS

CONSTITUENT	ORTHORHOMBIC PYROXENE		MONOCLINIC PYROXENE			ALKALI PYROXENE (AEGIRITE SERIES)	
	Feldspar-free Ultrabasic and Basic Igneous Rocks	Gabbros and Norites	Pyroxenites, Lherzolites, Etc.	Gabbros and Norites	Augite Syenites and Augite Diorites	Alkalie Granites and Alkalie Syenites	Nepheline Syenites
No. of analyses .	19	10	7	30	6	9	22
SiO ₂	54.46	51.02	49.04	50.39	49.76	51.56	49.83
Al ₂ O ₃	2.40	3.84	4.65	3.95	5.04	2.26	2.31
Fe ₂ O ₃	0.53	1.37	1.49	1.73	3.28	19.95	24.20
FeO	8.07	15.47	5.08	9.20	7.46	7.07	6.02
MnO	0.07	0.40	0.17	0.19	0.30	0.76	0.62
MgO	31.52	21.59	17.60	15.15	12.55	2.66	1.55
CaO	1.72	5.70	20.19	17.82	18.89	6.60	4.17
Na ₂ O	0.15	0.20	0.05	0.18	1.24	8.39	10.37
K ₂ O		0.04	0.02	0.09	0.09	0.39	0.57
H ₂ O		0.27	1.44	0.82	0.73	0.32	0.32
TiO ₂	0.04	0.01	0.13	0.51	0.01	0.19	0.35
Cr ₂ O ₃	0.18	n.d.	0.23	0.07	n.d.	n.d.	n.d.
Total	99.90	99.91	100.09	100.10	99.35	100.15	100.31

Among the pure Fe²⁺-Mg²⁺ pyroxenes the monoclinic species are rare constituents of igneous rocks. The orthorhombic pyroxenes, enstatite and hypersthene, are the more common and consequently geochemically the more important pyroxenes. They are found particularly in ultrabasic igneous rocks and in the basic and acidic rocks of the mangerite type of crystallization (see under "Sequence of Crystallization," p. 164). The enstatite-hypersthene series is of interest from the crystal chemical viewpoint, inasmuch as the ferrous end-member, Fe₂[Si₂O₆], does not seem to be stable in conditions prevailing during the main stage of crystallization of magmas. The structure of the magnesian end-member, Mg₂[Si₂O₆], or enstatite, on

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the other hand, is very stable, and therefore rather pure enstatite is often found as a constituent of ultrabasic igneous rocks. However, the study of the system FeO-SiO_2 shows that the binary compound $\text{FeO} \cdot \text{SiO}_2$ does not crystallize from the melt (Bowen and Schairer, 1932). Pure ferrous metasilicate, which occurs as the monoclinic clinoferrosilite, has been found in the lithophysae of an obsidian in Kenya in East Africa, but here it evidently was produced at a low temperature and probably is rather unstable.

The instability of the pure ferrous end-member in the enstatite-hypersthene series causes the petrologically and geochemically important members of this series to be regularly rich in magnesium. In

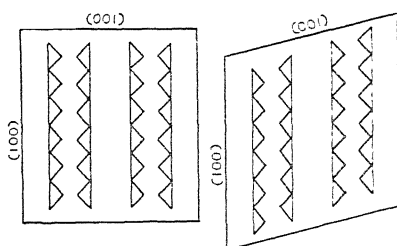


FIG. 5.6.—Structure of the orthorhombic and monoclinic pyroxenes, diagrammatically presented.

the orthorhombic pyroxenes of ultrabasic and basic igneous rocks the atomic $\text{Mg}:\text{Fe}$ ratios, calculated from Table 5.22, are the following:

	$\text{Mg} \text{ Fe}$	
Orthorhombic pyroxenes from ultrabasic igneous rocks.....	6.69	.
Orthorhombic pyroxenes from gabbros and norites.....	2.45	

The molecular content of the ferrous component in hypersthene of common igneous rocks may be as high as 50 per cent, but in some hypersthene the content is still higher. The iron-rich members of the series usually contain notable quantities of manganese, and it is possible that such irrelevant additions cause the crystallization of the iron hypersthene as stable structures.

The diopside-hedenbergite series is derived from the pure ferromagnesian pyroxenes by the substitution of one Fe^{2+} or Mg^{2+} ion by Ca^{2+} . Unlike the enstatite-hypersthene series, both end-members in the new series are stable. They are common constituents of igneous and contact metamorphic rocks. Diopside forms with clinoenstatite a series of isomorphous mixtures, the members of which occur as the

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common pigeonite in volcanic rocks. Johannsenite is a mineralogical curiosity.

The three alkali pyroxenes—jadeite, aegirite, and spodumene—may be derived by the substitution of Mg^{2+} - Mg^{2+} or Ca^{2+} - Mg^{2+} by Na^{+} - Al^{3+} , Na^{+} - Fe^{3+} , or Li^{+} - Al^{3+} , respectively, whereby the electric balance of the structure is maintained. These minerals, even though interesting from the crystal chemical viewpoint, are geochemically of minor importance. The Na^{+} - Al^{3+} pyroxene jadeite seems to be unstable under the circumstances commonly prevailing during magmatic crystallization. According to prevalent opinion, jadeite cannot form except under high pressures. The Na^{+} - Fe^{3+} pyroxene aegirite forms promptly when the atomic abundance of sodium in the rock melt exceeds the atomic abundance of aluminum; the complete removal of sodium in feldspars is then no longer possible. The Li^{+} - Al^{3+} pyroxene spodumene is a common constituent of granite pegmatites, and its formation affords proof of the instability of the lithium feldspar structure.

All the pyroxenes discussed above are geochemically less important than are the members of the augite series. The various augites, which are of complex chemical composition, belong to the most important mafic constituents of igneous rocks.

AMPHIBOLES

The general formula of the amphiboles presented in a previous paragraph shows that the amphiboles are chemically more complicated than the pyroxenes. The number of possible diadochic substitutions in the amphibole group is greater than in the pyroxene group. Therefore, as simple formulas cannot be presented for the amphiboles as were those given for the pyroxenes. Both orthorhombic and monoclinic amphiboles are known, and they show structural relationships similar to those found in the corresponding pyroxenes.

Many amphiboles either are totally absent in primary igneous rocks or occur only as minerals of secondary origin therein. The most important primary amphiboles of the igneous rocks are the magnesium-poor riebeckites and the silica-poor basaltic and common hornblende. The hornblendes, because of their frequent occurrence, are geochemically the most important amphiboles. Amphiboles belonging to the riebeckite series are met only in alkalic rocks.

The average chemical composition of amphiboles from some igneous rocks is given in Table 5.23. The values are from Chirvinsky

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(1931). In typical potash-rich granites the Fe:Mg ratio of the hornblende differs from the average given by Chirvinsky. The composition of the hornblende from the rapakivi granite at Uksunjoki in the Salmi area in eastern Fennoscandia is presented in Table 5.24 to illustrate the difference. The analysis of this extremely iron-rich amphibole is from Sahama (1947).

In the amphiboles, up to one-fourth of the Si^{4+} ions in the $[\text{SiO}_4]$ tetrahedra may become replaced by Al^{3+} . The substitution takes

TABLE 5.23
AVERAGE CHEMICAL COMPOSITION (IN PER CENT BY WEIGHT)
OF AMPHIBOLES FROM SOME IGNEOUS ROCKS

CONSTITUENT	AMPHIBOLE FROM—				
	Calc-alkalic			Alkalic	
	Gabbros and Norites	Diorites	Granites	Granites	Syenites and Nepheline Syenites
No. of analyses	10	24	9	4	23
SiO_2	44 88	45 83	47 99	49 29	41. 41
Al_2O_3	10. 83	10. 13	6 27	2 26	7. 55
Fe_2O_3	4 85	4. 73	3 24	18. 70	8 21
FeO	10 19	10 59	11 23	17 12	22 19
MnO	0 09	0 15	0 25	1 25	0 85
MgO	12 87	13 28	14 18	0 55	2 95
CaO	12 18	11. 43	12 91	2 51	7. 61
Na_2O	1 44	1 58	1 69	6 79	4 48
K_2O	0 39	0. 48	0 67	0 56	1 79
H_2O	1 49	1 32	0 97	0 88	1 02
TiO_2	0. 80	0 34	0. 46	0 32	1 64
P_2O_5	n.d.	n.d.	0 04	n.d.	0 11
F	n.d.	0 06	0 03	0 05	0 06
Total ..	100 01	99. 92	99 93	100 28	99 87

place particularly in basaltic and in common hornblende, which consequently resemble augite in this respect.

A comparison of Tables 5.22 and 5.23 shows that augite and hornblende do not correspond to each other as far as their bulk chemical composition goes. The most conspicuous difference is the higher content of aluminum and iron, the lower content of calcium, and the somewhat lower content of magnesium in the hornblende.

OLIVINES

The members of the forsterite-fayalite series are the geochemically most important olivines. Like the feldspathoids, these minerals occur

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as principal constituents of some igneous rocks. In the upper lithosphere their total amount certainly is smaller than the quantity of the pyroxenes and the amphiboles. Therefore, the olivines were not included in the average mineralogical composition of the igneous rocks presented in Table 5.16.

Structurally, the olivines probably afford the best example of silicates containing independent $[\text{SiO}_4]$ tetrahedra which share no oxy-

TABLE 5.24
CHEMICAL COMPOSITION OF AMPHIBOLE FROM RAPA-
KIVI GRANITE AT UUKSUNJOKI, SALMI AREA,
EASTERN FINNOSCANDIA

Constituent	Per Cent by Weight
SiO_2	38.24
Al_2O_3	10.17
Fe_2O_3	5.00
FeO	26.64
MnO	0.28
MgO	1.07
CaO	10.64
Na_2O	1.50
K_2O	1.57
$\text{H}_2\text{O}+$	1.88
$\text{H}_2\text{O}-$	0.08
TiO_2	2.00
F.....	1.06
Cl.....	0.51
	100.64
Less O for F and Cl.....	0.57
Total.....	100.07

gen ions with the neighboring tetrahedra. The pure end-members of the olivine group are the following:

Forsterite, $\text{Mg}_2[\text{SiO}_4]$
Fayalite, $\text{Fe}_2[\text{SiO}_4]$
Tephroite, $\text{Mn}_2[\text{SiO}_4]$

These components form isomorphic mixtures. For the forsterite-fayalite series Deer and Wager (1939) have suggested a nomenclature which is presented in Table 5.25. Their terminology is adopted in this book. A complete series of solid solutions between forsterite and fayalite occurs in Nature. In ultrabasic rocks, such as dunites, the olivine is mostly rich in magnesium and contains about 10 per cent of the Fe_2SiO_4 molecule. The iron-rich varieties are constituents of metasomatic ultrabasic rocks, of some diabbases, and of other rocks that give proof of extreme differentiation. It is highly probable that the iron-rich varieties are more frequent rock-making minerals than

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are the magnesium-rich types. Geochemically, the most abundant olivines probably are hyalosiderites. In petrographic descriptions the name olivine is often used without a determination of the composition.

TABLE 5.25
NOMENCLATURE OF FORSTERITE-FAYALITE SERIES

Compound	Molecular Percentage of Fe_2SiO_4
Forsterite (Fo)	0- 10
Chrysolite	10- 30
Hyalosiderite	30- 50
Hortonolite	50- 70
Ferrohortonolite	70- 90
Fayalite (Fa)	90-100

TABLE 5.26
AVERAGE COMPOSITION (IN PER CENT BY WEIGHT) OF
OLIVINE FROM SOME IGNEOUS ROCKS

CONSTITUENT	OLIVINE FROM—		
	Peridotites	Gabbros and Norites	Intermediate and Acidic Rocks
No. of analyses	13	5	5
SiO_2	40 04	34 24	30 83
Al_2O_3	0 81	1 49	n.d.
Fe_2O_3	0 47	1 00	1 06
FeO	11 33	37 70	63 18
MnO	0 23	0 15	2 05
MgO	45 64	23 62	1 10
CaO	0 19	0 33	0 15
Na_2O	} 0 06	0 13	} 0 08
K_2O		0 04	
H_2O	0 42	0 14	0 21
Cr_2O_3	0 08	n.d.	n.d.
NiO	0 02	0 04	n.d.
TiO_2	0 38	0 88	0 24
Insoluble	0 12	n.d.	0 78
Total	99 79	99 76	99 68

Tephroite is mostly found in metasomatic rocks and in manganese deposits. An isomorphic mixture of tephroite and fayalite (with forsterite) is called knebelite. Other minerals of the olivine group, viz., monticellite, $\text{CaMg}[\text{SiO}_4]$, glaucochroite, $\text{CaMn}[\text{SiO}_4]$, and larsenite, $\text{PbZn}[\text{SiO}_4]$, are not found in igneous rocks and are rare.

The average chemical composition of olivine from some igneous rocks is presented in Table 5.26, based on Chirvinsky (1931), which illustrates the predominance of the magnesium-rich olivines in basic

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rocks and of the iron-rich types in intermediate and acidic igneous rocks. The change in the Mg:Fe ratio in olivine is analogous to the change in the Mg:Fe ratio in the orthorhombic pyroxenes discussed in the preceding paragraph.

QUARTZ

The different modifications of silica are presented in Table 5.27. Among the minerals listed, quartz is by far the most important in the upper lithosphere. Tridymite and cristobalite are only mineralogical curiosities, which are met particularly in lavas and in volcanic sublimes. The isometric high-cristobalite has also been found in opals. Owing to the readiness of its low-high transition, quartz occurs in the low-temperature form in igneous rocks.

TABLE 5.27
THE CRYSTALLINE MODIFICATIONS OF SILICA

Mineral	System	Stability Range in ° C.
Quartz	Trigonal	< 573
	Hexagonal	573-867
Tridymite.	Orthorhombic	< 105
	Hexagonal	105-160
	Hexagonal	160-1,470
Cristobalite.	Orthorhombic	< 200-270
	Isometric	From 200-270 to 1,728

Structurally, quartz has a continuous three-dimensional framework of $[\text{SiO}_4]$ tetrahedra. In the direction of the crystallographic *c*-axis, the silicon atoms are found to be arranged in the manner indicated in Figure 5.7 (according to Bragg, 1937). The structure indicates the lack of any cleavage in quartz. Along with the chemical resistance of quartz to weathering, this circumstance is important for the geochemistry of sediments (see under "Weathering," p. 191).

The existence of free silica in the form of quartz in igneous rocks is a result of the high abundance of silicon in the upper lithosphere. On an average, silica is in excess over the oxides of metals. If the abundance ratio were the reverse, silica and the oxides would have reacted and silicates would have formed.

MICAS

The mica group includes a number of structurally similar minerals which may be divided into two general subgroups, viz.,

1. The calcium-free micas: $\text{Me}_2^+[(\text{OH})_2] \text{AlSi}_3\text{O}_{10}]$
2. The calcium-bearing micas: $\text{Me}_3^+[(\text{OH})_2] \text{Al}_2\text{Si}_2\text{O}_{10}]$

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The calcium-free micas are the dominant types in rocks. In them, as in the alkali feldspars, one of the Si^{4+} ions is replaced by Al^{3+} , whereas in the calcium-bearing micas two Si^{4+} ions are replaced by Al^{3+} . Consequently, the degree of silicification in the micas corresponds to that in the feldspars. All the micas are aluminosilicates, but usually aluminum ions in 6-co-ordination are also found outside the silicon-oxygen network.

The most important micas are the following:

Muscovite,	$\text{KAl}_2[(\text{OH},\text{F})_2] \cdot \text{AlSi}_3\text{O}_{10}$
Phlogopite,	$\text{KMg}_3[(\text{F},\text{OH})_2] \cdot \text{AlSi}_3\text{O}_{10}$
Biotite,	$\text{K}(\text{Mg},\text{Fe},\text{Mn})_2[(\text{OH},\text{F})_2] \cdot \text{AlSi}_3\text{O}_{10}$
Paragonite,	$\text{NaAl}_2[(\text{OH},\text{F})_2] \cdot \text{AlSi}_3\text{O}_{10}$
Margarite,	$\text{CaAl}_2[(\text{OH})_2] \cdot \text{Al}_2\text{Si}_2\text{O}_{10}$

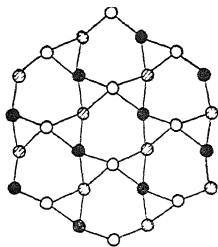


FIG. 5.7.—Structure of low-temperature (β -)quartz. The direction of the c -axis is perpendicular to the plane of the paper. Only the Si^{4+} ions are indicated in the figure. (Based on material from *Atomic Structure of Minerals*, by W. L. Bragg, 1937. Courtesy of Cornell University Press.)

Biotite is the most common mica in igneous rocks, as Table 5.16 shows. The other micas do not belong to the minerals formed during the main stage of crystallization, with the exception of some muscovite found in granites. Paragonite and margarite are rare.

Some varieties of mica are known which are characterized by the presence of considerable quantities of certain trace elements. They include, among others,

- the lithian micas lepidolite and zinnwaldite
- the barian muscovite öllacherite
- the chromian mica fuchsite
- the vanadoan mica roscoelite
- the manganoan biotite manganophyllite
- the titanian biotite wodanite

The structure of muscovite is presented in Figure 5.8, which is based on Bragg (1937). Structurally, the micas may be derived from the amphiboles by linking infinite double chains to form two-dimen-

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sional networks or sheets in which the $[\text{SiO}_4]$ tetrahedra share three of their four O^{2-} ions with the neighboring tetrahedra. In a sheet all free vertices of the tetrahedra point in the same direction. The struc-

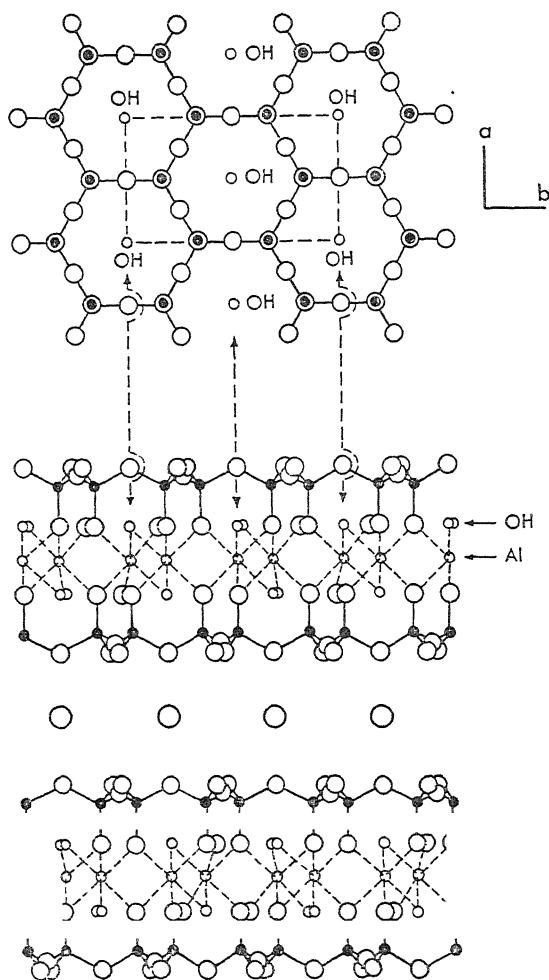


FIG. 5.8.—Structure of muscovite. (Based on material from *Atomic Structure of Minerals*, by W. L. Bragg, 1937. Courtesy of Cornell University Press.)

tures of the other micas may be derived from the structure of muscovite, in which two two-dimensional sheets of silicon-oxygen tetrahedra are placed together, with the vertices of the tetrahedra pointing inward. The vertices are linked with Al^{3+} ions, which are 6-co-ordinated by four O^{2-} ions of the sheets and by two OH^- or F^- ions. The OH^- and F^- ions are located in the centers of the hexagons formed

by the free vertices of the tetrahedra. The neighboring complex sheets are linked by 12-co-ordinated K^+ ions, situated in large cavities in the structure. With reference to their total symmetry, the micas either are monoclinic or triclinic because the two-dimensional double sheets are somewhat displaced. The eminent cleavage parallel to the basal plane in many micas is the result of the rupture of the weak $O^{2-}-K^+$ bonds which hold the double sheets together.

The possibilities of diadochic replacement in the micas are numerous, just as in the pyroxenes and the amphiboles. However, there is a substantial difference between the pyroxenes and the micas in this respect. In the pyroxenes the substitution takes place ion by ion, and the electric neutrality of the structure is maintained by many simultaneous substitutions. The number of ions in the structure consequently remains unchanged. In the micas, on the other hand, the manner of substitution is different. In the muscovite structure only a part of the positions of the Al^{3+} ions are occupied. Therefore, when biotite or phlogopite is derived from muscovite, the substitution takes place charge by charge. Two Al^{3+} ions are replaced by three Mg^{2+} , Fe^{2+} , or Mn^{2+} ions. The number of the ions increases by one, but the sum of the electric charges of the ions remains unchanged. The extra cation introduced into the muscovite structure will occupy an empty position in the structure, and no material structural change will result. When margarite is derived from muscovite, the degree of silicification will decrease in a manner analogous to the decrease when passing from albite to anorthite.

The average composition of biotite and muscovite from granites and granite pegmatites is presented in Table 5.28. The values are from Chirvinsky (1931).

ACCESSORY CONSTITUENTS OF IGNEOUS ROCKS

The most frequently occurring accessory silicate minerals in common igneous rocks are zircon, $Zr[SiO_4]$, and sphene (also called titanite), $CaTi[(O,OH,F)|SiO_4]$.

Zircon is the most abundant of all zirconium minerals and contains most of the zirconium present in the upper lithosphere. Its structure contains independent $[SiO_4]$ tetrahedra, which are linked together by Zr^{4+} ions in 8-co-ordination. The zircon structure appears less stable than is often assumed (Machatschki, 1941). This circumstance, which is the result of the relatively small size of the Zr^{4+} ion (radius 0.87 kX), affects the manner of occurrence of zirconium in igneous

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rocks and probably is the cause of the strong enrichment of zirconium in acidic rocks. Zircon is isotypic with xenotime. Zircons of low specific gravity are partly amorphous as the result of radioactive decomposition of their structure. The reason for the decomposition is the presence of thorium, which diadochically replaces zirconium. Such zircons are called zirconoids.

Also sphene has independent $[\text{SiO}_4]$ tetrahedra in its structure. In addition, O^{2-} ions, partly replaced by OH^- and F^- , are situated out-

TABLE 5.28
AVERAGE CHEMICAL COMPOSITION (IN PER CENT
BY WEIGHT) OF BIOTITE AND OF MUSCOVITE

Constituent	Biotite from Granites and Granite Pegmatites	Muscovite from Granites and Granite Pegmatites
No. of analyses.....	51	37
SiO_2	36 46	44 95
Al_2O_3	17 15	33 51
Fe_2O_3	8 17	1 76
FeO	14 46	0 64
MnO	0 56	0 05
MgO	8 70	0 81
CaO	0 98	0 37
Na_2O	0 91	1 32
K_2O	8 23	10 47
H_2O	2 87	5 30
TiO_2	1 25	0 41
F	0 18	0 13
Total	99 92	99 72

side the silicon-oxygen tetrahedra (Sahama, 1946; Jaffe, 1947). The sphene structure shows considerable deviation from electrostatic neutrality (Zachariasen, 1930). In some nepheline syenites the corresponding sodium mineral ramsayite, $\text{Na}_2\text{Ti}_2[(\text{O},\text{OH},\text{F})](\text{SiO}_4)_2$, plays the petrographic role of sphene. Sphene and ramsayite are not isomorphic.

Apatite, $\text{Ca}_5[(\text{F},\text{Cl},\text{OH})](\text{PO}_4)_3$, is the most abundant phosphate mineral of igneous rocks. The $[\text{PO}_4]$ tetrahedra in the apatite structure are partly replaced by $[\text{SiO}_4]$, $[\text{SO}_4]$, $[\text{AsO}_4]$, and $[\text{VO}_4]$ tetrahedra. In addition, calcium may be replaced by sodium, lead, manganese, and other metals. Like the pair zircon-xenotime, the apatites also have a structure in which the $[\text{SiO}_4]$ and $[\text{PO}_4]$ tetrahedra replace each other. Among the diadochic substitutions in the apatite group,

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the mutual replacement between Cl^- and F^- is remarkable. The two anions differ considerably from each other in size. As a matter of fact, the positions of the F^- and Cl^- ions in the unit cell are not identical but differ by one-fourth the length of the unit cell in the direction of the c -axis.

Other accessory phosphate minerals of igneous rocks include monazite, $\text{Ce}[\text{PO}_4]$, and xenotime, $\text{Y}[\text{PO}_4]$. The two minerals, not isomorphic with each other, occur mostly in acidic rocks.

Among the fluorides only fluorite, CaF_2 , is geochemically important as a constituent of igneous rocks.

TABLE 5.29
AVERAGE CHEMICAL COMPOSITION (IN PER CENT
BY WEIGHT) OF CHROMITE AND ILMENITE

Constituent	Chromite from Ultrabasic Rocks	Ilmenite from Gabbros and Norites
SiO_2	1 08	0 24
Al_2O_3	15 65	0 10
Fe_2O_3	2 32	20 92
Cr_2O_3	50 38	0 09
FeO	17 47	31 25
MnO	0 29	0 07
MgO	12 80	1 88
CaO	n.d.	0 37
TiO_2	0 13	44 79
Total	100 12	99 71

Among the accessory oxide minerals found in igneous rocks, the following are important: ilmenite, FeTiO_3 ; magnetite, Fe_3O_4 ; and chromite, FeCr_2O_4 . Chromite occurs mostly in ultrabasic rocks, whereas ilmenite and magnetite are common in all kinds of igneous rocks. On an average, magnetite is more abundant than ilmenite. The average composition of chromite and ilmenite is presented in Table 5.29. The analyses are from Chirvinsky (1931).

The most abundant accessory sulfide minerals of igneous rocks are pyrite, FeS_2 ; pyrrhotite, $\text{FeS-Fe}_3\text{S}_8$; chalcopyrite, CuFeS_2 ; pentlandite, $(\text{Fe,Ni,Co})_9\text{S}_8$; and bornite, Cu_5FeS_4 . These minerals are mentioned here in the order of their relative abundance (Newhouse, 1936; Ramdohr, 1940).

CHEMICAL DIFFERENTIATION OF IGNEOUS ROCKS

It is assumed that the original silicate crust of the Earth was chemically rather homogeneous. The igneous rocks, however, are

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chemically widely variable, and rocks with a chemical composition similar to the average composition of igneous rocks are rare. Therefore, the assumption follows that the igneous rocks are products of an extensive chemical differentiation in the Earth's crust. This differentiation process is the second geochemical differentiation of Goldschmidt (1926, 1929, 1933*b*); the first geochemical differentiation comprises the processes that led to the formation of the concentric structure of the Earth.

The average chemical composition of igneous rocks (upper lithosphere) and that of plateau basalts form the basis of the survey of the second geochemical differentiation. It is commonly believed that the plateau basalts represent original undifferentiated Sialma material which has reached the Earth's surface as fissure eruptions. Consequently, the plateau basalts represent a parental magma that differentiated to produce all primary magmatic rocks present in the upper lithosphere.

The average chemical composition of the plateau basalts, compared with the average composition of all basalts and of all igneous rocks, is presented in Table 5.30 on the basis of the calculations of Daly (1933) and of Clarke and Washington (1924; from Table 2.1).

Equilibrium is established in a differentiating magma in constant external conditions, but departures from equilibrium are frequent as soon as the external conditions—e.g., temperature—change. A series of processes leading to changes in chemical composition takes place in a crystallizing magma as a result of decrease in temperature. However, these processes are discussed in treatises on petrology and will not be considered here. Only the general principles of differentiation are of immediate interest in geochemistry and will be presented, shortly and schematically, in the following paragraphs.

Geochemically, it is important to follow the changes of chemical composition of the products formed during magmatic differentiation, that is, the distribution of the elements among the products of differentiation and the physicochemical rules governing the distribution. However, most of the processes taking place in Nature are far more complicated than their counterparts and imitations in the laboratory. The difference is caused, among others, by the presence of volatile constituents in the natural rock melts and by the assimilation phenomena in the already solidified rocks that surround a magma reservoir.

The chemical differentiation in a natural rock melt of plateau-ba-

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saltic composition, for example, starts with the separation of magnesium and silica in olivine (forsterite, $\text{Mg}_2[\text{SiO}_4]$). Because of their high specific gravity, the olivine crystals sink to the bottom of the magma reservoir or are assembled by magmatic currents. They are concentrated locally in the form of dunites or olivinites. In a similar manner calcium, aluminum, and silicon may become separated as calcic plagioclase, which forms the anorthosite bodies. The molten sulfides will thereafter separate from the magma. The miscibility of silicate and sulfide melts is limited, and Vogt's (1918) results of an

TABLE 5.30
AVERAGE CHEMICAL COMPOSITION (IN PER CENT BY WEIGHT) OF
ALL BASALTS, PLATEAU BASALTS, AND
AVERAGE IGNEOUS ROCK*

Constituent	Plateau Basalts	All Basalts	Average Ig- neous Rock
No. of analyses.	43	198	5,159
SiO_2	48.80	49.06	59.14
Al_2O_3	13.98	15.70	15.34
Fe_2O_3	3.59	5.38	3.08
FeO	9.78	6.37	3.80
MnO	0.17	0.31	0.12
MgO	6.70	6.17	3.49
CaO	9.38	8.95	5.08
Na_2O	2.59	3.11	3.84
K_2O	0.69	1.52	3.13
H_2O	1.80	1.62	1.15
TiO_2	2.19	1.36	1.05
P_2O_5	0.33	0.45	0.30
Total	100.00	100.00	99.52

* Based in part on material from *Igneous Rocks and the Depths of the Earth*, by R. A. Daly. Copyright 1933. Courtesy of McGraw-Hill Book Co.

investigation of silicate slags from ore-smelting furnaces showed that the solubility decreases with decreasing temperature. The separated sulfide melt, upon crystallization, will give mainly pyrrhotite, $\text{FeS-Fe}_5\text{S}_6$, and pentlandite, $(\text{Fe,Co,Ni})_9\text{S}_8$, which is the most important ore mineral of nickel. Almost contemporaneously with, or immediately after, the crystallization of olivine, the bulk of titanium is separated as ilmenite, FeTiO_3 ; much iron as magnetite, Fe_3O_4 ; and often chromium as chromite, FeCr_2O_4 . The titaniferous and chromiferous iron ores are thereby formed; they are the last rocks to be included in the group of the early magmatic crystallates.

The second step in the differentiation is the main stage of magmatic crystallization. The igneous rock series, starting with gabbro

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and ending with granite, is the product of fractional crystallization during this stage. One after another, the crystal structures become stable and separate in the order of their stability. The condition of the differentiation is the removal of the crystallizing minerals, whereby reactions between the crystals and the residual magmas are prevented. The crystals are removed by means of gravity either by sinking or by rising or by means of the separation of the residual magma by the squeezing-out or filter-press mechanism.

All natural magmas contain varying amounts of volatile constituents, which, as mineralizers, have a notable, or even a decisive, effect on the course of crystallization. During the early magmatic stage of differentiation, only little volatile matter is separated. Even though the formation of minerals containing volatile constituents is notably promoted during the subsequent stages of crystallization, the bulk of the volatile compounds becomes enriched in the residual melts and solutions. When the concentration of the volatile constituents reaches a certain limit, the main stage of crystallization ends, and the late magmatic stage sets in. This latter stage of crystallization is characterized by the fact that a relatively insignificant drop in temperature is enough to cause the crystallization of the bulk of the residual melt, which is rich in mineralizers. Provided that the rate of decrease of temperature remains constant during the crystallization, the rate of crystallization must increase abruptly and considerably at the onset of the late magmatic stage, i.e., during the crystallization of the pegmatites. The lack of idiomorphism often displayed by quartz and feldspar of pegmatites affords proof of their rapid separation. The change in the rate of crystallization causes an abrupt enrichment in water and other volatile substances in the residual magma, and consequently the crystallization residue during the subsequent pneumatolytic stage of crystallization is a supercritical aqueous solution rather than a melt.

The pneumatolytic and hydrothermal stages differ essentially from each other in so far as the pneumatolytic liquors are supercritical, i.e., they crystallize at temperatures above the critical temperature of water vapor, whereas the crystallization temperature of the hydrothermal solutions is below it. During these stages, especially in the hydrothermal stage, the rate of crystallization decreases as shown, e.g., by the well-developed crystals often found in cavities in rocks and in mineral veins.

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The general course of the crystallization of a calc-alkalic basaltic magma is as follows:

Early magmatic stage	{ Silicates (dunite, anorthosite) Sulfides (pyrrhotite-pentlandite paragenesis) Oxides (ilmenite, chromite, magnetite)
Main stage	{ Gabbros Diorites Granites
Late magmatic stage	{ Pegmatites Pneumatolytic deposits Hydrothermal deposits
Volcanic emanations	

The boundaries between the different stages are not very rigid because the different steps are parts of a continuous process and all are essential parts of the magmatic differentiation by crystallization.

In the proximity of the Earth's surface, where the tension of the volatile constituents of the magma exceeds the external pressure, a part of the volatiles are released in the form of volcanic emanations and will directly participate in the exogenic cycle of matter.

EARLY MAGMATIC SULFIDES

The early magmatic sulfides separate from the magma as a melt and form, upon their crystallization, sulfide mineral bodies that belong to the pyrrhotite-pentlandite paragenesis, which is the only known representative of the early magmatic sulfides. Most sulfide ore bodies belonging to the pyrrhotite-pentlandite assemblage have, after their formation, participated in complicated geological processes, and therefore their original manner of formation is established only with difficulty.

The average chemical composition of the early magmatic sulfides is presented in Table 5.31 on the basis of an analysis of a composite mixture of sulfide minerals made by Noddack and Noddack (1931a; see also Table 5.2). The analyzed mixture consisted of 35 pyrrhotites, 10 primary pyrites, 8 pentlandites, and 4 nickelian pyrites from a number of localities.

The composite mixture differs chemically from the late magmatic pneumatolytic and hydrothermal sulfides and actually, in some essential features, resembles the average composition of the sulfide phase of the meteorites, its closest genetic counterpart. For comparison, the average composition of the sulfide phase of the meteorites is

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presented in Table 5.31, according to the analyses and estimates of Noddack and Noddack (1930: values of S, Zn, Mn, Se, As, V, Mo, Cd, Te, W, Bi, Sb, Tl, In, Cr, Hg, and Re) and of Goldschmidt (1937*b*: the other elements). However, important chemical differ-

TABLE 5.31
AVERAGE COMPOSITION OF EARLY MAGMATIC SULFIDES
AND OF SULFIDE PHASE OF METEORITES

Element	Composite of Early Magmatic Sulfide Minerals (g/ton)	Sulfide Phase of Meteorites (Troilites) (g/ton)
Fe.....	539,000	630,000
S.....	404,000	343,000
Ni.....	31,400	1,000
Cu.....	10,900	100-600
Zn.....	8,500	1,530
P.....	2,500	3,000
Co.....	2,100	100
Mn.....	800	460
Se.....	200	840
Pb.....	100	20
As.....	60	1,020
Sn.....	50	15
V.....	40	45
Mo.....	20	11
Cd.....	20	30
Ag.....	10	18
Ge.....	10	30
Pd.....	4	2
Ga.....	2	8
Te.....	2	17
W.....	2	Present
Pt.....	2	2
Bi.....	2	2
Ru.....	1	9
Sb.....	1	7 8
Tl.....	1	0 3
In.....	0 7	0 8
Ir.....	0 4	0 4
Rh.....	0 3	0 4
Au.....	0 2	0 5
Os.....	0 1	9
Cr.....	0 02	1,200
Hg.....	0 02	Present
Re.....	0.02	0 001

ences also exist between the two analyses. The atomic Fe:S ratios differ; in the sulfides of the meteorites the ratio is about 1:1, whereas the value for the early magmatic sulfides is about 5:6. The crystal chemical explanation of the difference is that pyrrhotite predominates in the early magmatic sulfides, but troilite is present in the meteorites. Mineralogically, pyrrhotite and troilite are identical, and they both have structures of the nickel arsenide type. Many minerals

of this type are characterized by strongly metallic properties and by a chemical composition which does not closely follow stoichiometric rules. Pyrrhotite analyses, as a rule, show an excess of sulfur over that expressed by the formula of iron monosulfide, FeS , and the atomic sulfur content may be as high as 55.5 per cent. No such sulfur excess is present in troilite. The crystal structure of pyrrhotite, however, shows that there is no excess of sulfur but rather a deficiency of iron. Some positions of the Fe^{2+} ions in the structure are vacant, and a small number of Fe^{3+} ions is present to maintain the electric balance in the structure. Compared with the troilite structure, the pyrrhotite structure is disordered.

Table 5.31 also shows that nickel and cobalt are considerably more abundant in the early magmatic sulfides than in the sulfide phase of the meteorites. However, in the metal phase of the meteorites their content, viz., 84,900 g/ton Ni and 5,700 g/ton Co according to Goldschmidt (1937b), is much higher than in the early magmatic sulfides. The explanation of the remarkable behavior of nickel and of cobalt is that their general geochemical character is strongly siderophile. The metal phase is always present in the meteorites, and consequently the two metals become enriched therein, but in the upper lithosphere they become concentrated in sulfide minerals.

The content of copper in the early magmatic sulfides is very much higher than in the meteoritic sulfide phase. The sulfide bodies of the pyrrhotite-pentlandite paragenesis regularly contain notable amounts of copper, their average Ni:Cu ratio being 2:1. The explanation is that the general geochemical character of copper is mainly chalcophile, but in the meteorites copper has a notable siderophile tendency. In the upper lithosphere most of the copper is contained in sulfide minerals. Even the relatively small quantities of copper present in silicate rocks are combined with sulfur, chiefly in the form of chalcopyrite, CuFeS_2 .

Among the other elements listed in Table 5.31, zinc is strongly concentrated in the early magmatic sulfides. However, zinc is also enriched in late magmatic sulfides and in residual solutions formed during the crystallization of the early magmatic sulfides. Arsenic is abundant in the meteoritic sulfide phase, but in the terrestrial early magmatic sulfides its content is relatively low. The late magmatic sulfides are the proper surroundings of arsenic in the upper lithosphere. Chromium is strongly enriched in the sulfide phase of the meteorites, but in the early magmatic sulfides in the Earth its con-

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tent is remarkably low. This is due to the presence of daubréelite, FeCr_2S_4 , in the meteorites. In terrestrial surroundings daubréelite is unstable and promptly oxidizes. In the upper lithosphere, chromium does not possess noteworthy sulfophile properties.

EARLY MAGMATIC OXIDES

Unlike the early magmatic sulfides, the early magmatic oxides commonly are regarded as products of actual differentiation of a magma. In other words, when the crystallization of the magma starts, oxide minerals separate from the melt along with olivine. The early-separated oxides consist, mineralogically, of the oxide minerals frequently found in igneous rocks as accessory constituents. Titanian magnetite, ilmenite, and chromite are their main constituents. Titanian magnetite of plutonic rocks probably consists of exsolved ilmenite, magnetite, and hercynite (see chap. 21).

Chemically, the early-separated oxides are characterized by their titanium and chromium content. The titanium-rich crystallates occur preferentially in gabbros and in norites. They form the greatest known bodies of iron ore. However, the titanium content of the titaniferous iron ores largely prevents their utilization as a source of iron. The chromite bodies are genetically connected with ultrabasic rocks. Along with iron, titanium, and chromium, certain other metals are concentrated in the early magmatic oxides. They are discussed in Part II of this book.

SILICATES FORMED DURING THE EARLY AND MAIN STAGES OF CRYSTALLIZATION

SEQUENCE OF CRYSTALLIZATION

The chief rock-making constituents of igneous rocks consist of a number of felsic (light) and mafic (dark) silicate minerals. According to Table 5.16, the light constituents are by far the most abundant ones. They include the feldspars, quartz, and the feldspathoids. The most important dark constituents are the pyroxenes, amphiboles, micas, and olivines. The crystallization of calc-alkalic rocks may be expressed by means of the reaction series which contains both the felsic and the mafic minerals (Bowen, 1922). The reaction series is presented in Figure 5.9. It is a somewhat modified statement of the normal sequence of crystallization of the calc-alkalic rocks.

It must be noticed that, throughout the right-hand branch which contains the light constituents, the framework of the Si-O-Al tetra-

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hedra in the minerals remains unchanged, whereas in the left-hand branch of the dark constituents the framework changes continually. If only the silicon-oxygen framework is considered and no attention is paid to the cations in the structures, the order of crystallization is the following:

Independent tetrahedra→Chains→Double chains→Sheets.

The general course of differentiation proceeds from ultrabasic rocks through basic and intermediate types to the acidic or silicic rocks largely as a result of fractional crystallization. The principal

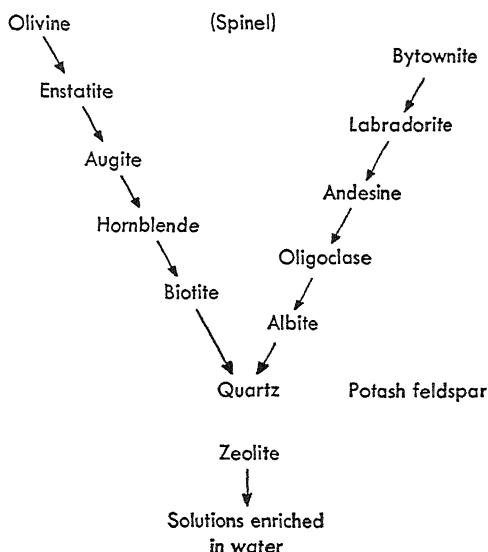


FIG. 5.9.—The reaction series

types of calc-alkalic rocks formed during magmatic crystallization are the following:

- 1a. Dunite: olivine (Harzburgite: olivine and enstatite)
- 1b. Anorthosite: calcic plagioclase
2. Gabbro: labradorite, augite (or hornblende)
3. Diorite: andesine, hornblende (or augite), biotite, quartz
4. Granite: quartz, oligoclase, hornblende, biotite, potash feldspar

The average chemical composition of the most important calc-alkalic rocks is presented in Table 5.32. The analyses are quoted from Daly (1933). With special reference to the composition of granite, it should be noticed that, along with typical granites, Daly's average also comprises somewhat more basic rocks that approach granodiorites in composition and rocks that have a trondhjemitic composition

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(see below). Therefore, Daly's granite average contains more sodium and less potassium than the typical granites. The composition of the potash-rich granites is illustrated by the average composition of rapakivi granites, presented in Table 5.33; the analysis is quoted from Sahama (1945*c*).

A chemical peculiarity of differentiation is the increase of the Fe:Mg ratio toward the later stages of crystallization. Magnesium

TABLE 5.32
AVERAGE CHEMICAL COMPOSITION (IN PER CENT BY WEIGHT) OF
CALC-ALKALIC IGNEOUS ROCKS*

Constituent	Dunites	Hornblendites	Gabbros	Diorites excluding Quartz Diorites	Granodiorites	Granites of All Periods
No. of analyses.	10	11	41	70	40	546
SiO ₂	40 49	42.80	48.24	56.77	65 01	70.18
Al ₂ O ₃	0 86	10 55	17 88	16 67	15 94	14.47
Fe ₂ O ₃	2 84	6 62	3 16	3.16	1.74	1.57
FeO	5 54	9.16	5 95	4 40	2.65	1.78
MnO	0 16	0 24	0.13	0.13	0.07	0.12
MgO	46.32	12.48	7.51	4 17	1.91	0.88
CaO	0 70	11 67	10.99	6.74	4 42	1.99
Na ₂ O	0 10	1 89	2 55	3 39	3.70	3.48
K ₂ O	0 04	1 00	0.89	2.12	2 75	4.11
H ₂ O	2 88	1.73	1.45	1.36	1 04	0.84
TiO ₂	0.02	1.62	0.97	0.84	0.57	0 39
P ₂ O ₅	0 05	0 24	0.28	0 25	0.20	0.19
Total	100.00	100 00	100 00	100.00	100.00	100.00

* Based on material from *Igneous Rocks and the Depths of the Earth*, by R. A. Daly. Copyright 1933. Courtesy of McGraw-Hill Book Co.

greatly predominates over iron in the early crystallized olivine. According to Table 5.32, the Fe:Mg ratio changes in the following way during the differentiation:

Rock	Fe Mg
Dunite	0.2
Gabbro	1.5
Diorite	2.4
Granite	4.9

The crystal chemical explanation of the change in the Fe:Mg ratio, according to Goldschmidt (1937*a*), is that an increase of the radius of the cation in a structure results in weakening the bonds therein, and consequently the melting point of the structure will decrease. Because the radius of Fe²⁺ (0.83 kX) is somewhat greater than the radius of Mg²⁺ (0.78 kX), the melting point of minerals of ferrous

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iron is lower than that of the corresponding magnesium minerals, and therefore magnesium is concentrated during the early stages of crystallization. The content of calcium reaches a maximum at the outset of the main stage of crystallization. Silicon, sodium, and potassium become enriched in the acidic rocks. The difference in the behavior of sodium and calcium is connected with the crystallization phenomena in the plagioclase series. The crystallization always begins with

TABLE 5.33
PARTIAL CHEMICAL COMPOSITION OF COMPOSITE
MIXTURE OF EASTERN FENNOSCANDIAN
RAPAKIVI GRANITES

Constituent	Per Cent by Weight
SiO ₂	72.58
Al ₂ O ₃	12.98
Fe ₂ O ₃	0.86
FeO.....	1.83
MnO.....	0.11
MgO.....	0.25
CaO.....	1.01
Na ₂ O.....	3.01
K ₂ O.....	5.28
H ₂ O+.....	0.66
H ₂ O-.....	0.38
TiO ₂	0.34
ZrO ₂	0.12
P ₂ O ₅	0.18
F.....	0.36
Cl.....	0.06
S (total).....	0.05
CO ₂	0.05
BaO.....	0.10
SrO.....	0.01
Rb ₂ O.....	0.16
Ga ₂ O ₃	0.01
Total.....	100.39

the separation of calcic plagioclase because the melting point of anorthite is considerably higher than that of albite. The order of crystallization in the plagioclase series may be understood in the following way: Both the Ca²⁺ ions of pure anorthite and the Na⁺ ions of pure albite occupy analogous structural positions. They are linked to O²⁻ ions. It is evident that the Coulomb attraction between Ca²⁺ and O²⁻ is stronger than in the pair Na⁺ and O²⁻. The bond between Ca²⁺ and O²⁻ is stronger than the bond between Na⁺ and O²⁻, and consequently the anorthite structure is stronger than the albite structure. Therefore, anorthite separates at an earlier stage of crystallization than albite does.

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The normal course of crystallization of calc-alkalic magmas is presented in Figure 5.10, according to Goldschmidt (1922*a*). However, the course of crystallization depends on the water content of the original melt. Magmas with a high content of mineralizers are often present in orogenic zones. If the water content is high, the crystallization will follow another course, and rocks belonging to the mica diorite type are formed. The crystallization diagram, according to Goldschmidt (1922*a*), is presented in Figure 5.11.

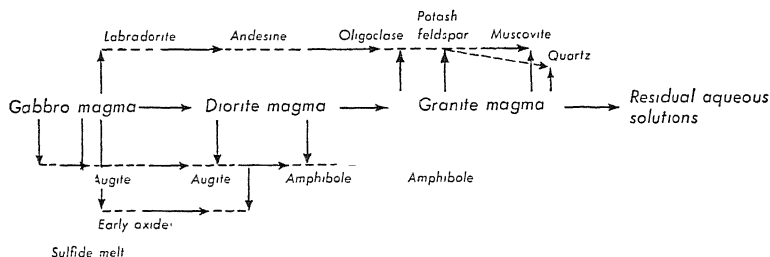


FIG. 5.10.—Normal course of crystallization of calc-alkalic magmas

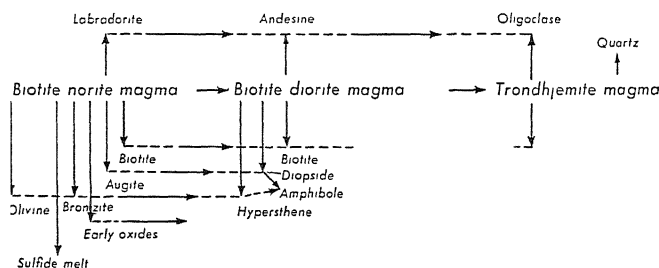


FIG. 5.11.—Course of crystallization of magmas rich in water (mica diorite type)

The main difference in crystallization between the normal and the water-rich magmas is that in the latter the separation of biotite starts earlier, at a considerably higher temperature, and that potash feldspar is very scarce or totally absent in them. The early crystallization of biotite is caused by the high water content of the melt. The bulk of potassium is removed in biotite during the early and intermediate stages of crystallization, and the lack of potassium in the later stages prevents the formation of notable amounts of potash feldspar. Therefore, albite by far predominates over potash feldspar in trondhjemites, but in other respects the trondhjemites correspond to granites.

If the water content of the original magma is exceptionally low, the crystallization will follow still another course (the mangerite type), which is presented, according to Goldschmidt (1922*a*), in Figure 5.12. This type of crystallization is characterized by the rather early start of the separation of potash feldspar. The separation of potassium from the melt at comparatively high temperatures consequently characterizes both the mica diorite type and the mangerite type.

CRYSTAL CHEMICAL DISCUSSION OF THE COURSE
OF CRYSTALLIZATION

The schematic course of crystallization discussed in the preceding paragraph is governed by the forces that tend to capture the constituents of mineral structures—ions in silicate structures—from the

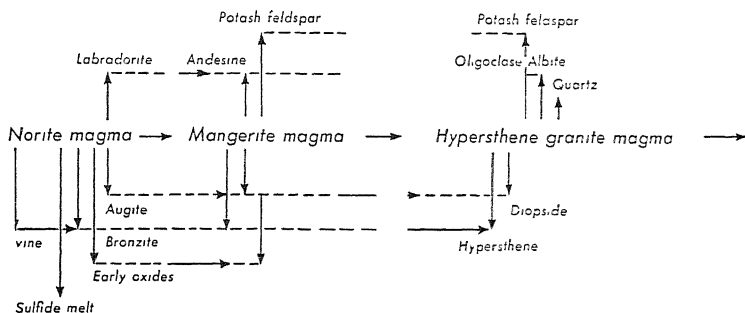


FIG. 5.12.—Course of crystallization of magmas poor in water (mangerite type)

melt with a low degree of order and to arrange them into a structure with a high degree of order. A silicate melt may be considered a solution in which each of the constituents acts as a solvent for the others. The ions contained in the melt constantly change their relative positions, and therefore the degree of order in the melt is low.

In a melt with a temperature close to the temperature of crystallization some kind of order is already present, even though it is not statistical, as in crystalline substances. Figure 5.13 shows the difference between the crystalline state and the statistically disordered state. The network of $[\text{SiO}_4]$ tetrahedra of a silicate and of the SiO_2 glass is presented in Figure 5.13 according to Zachariasen (1932). Even though the $[\text{SiO}_4]$ tetrahedra form a three-dimensional network in the glass, the structure lacks the regularity of the crystalline silicate. However, in both structures the co-ordination and the type of binding are essentially the same. The crystallization includes an abrupt transition from a disordered into an ordered state; in a silicate system, however, the transition is not very pronounced.

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The formation of minerals may be explained by means of kinetic reasoning with temperature as an essential function, as Wickman (1943) has done. When the temperature of a mineral structure is higher than absolute zero, the ions and atom groups oscillate about their mean regular positions. With increasing temperature, the oscillation intensity of an ion increases and may exceed a certain critical value. Thereupon, the ion will move from its original co-ordination into another co-ordination, and a new modification of the structure will form which is stable at the new temperature. The ion may also leave the original co-ordination altogether, i.e., the melting point

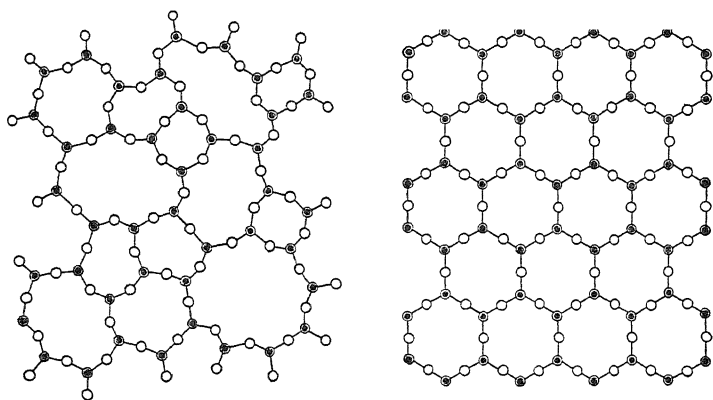


FIG. 5.13.—Structural difference between a silicate glass (a) and a crystalline silicate (b). (Based on material from the *Journal of the American Chemical Society*, Vol. 54, 1932. Used by permission.)

of the structure is reached. The energy required to move an ion from a position with a given co-ordination to another position with a different co-ordination is called the activation energy of the migration of the ion, or the E -value. The energetic stability of a structure is the sum of the migration energies of its constituting ions.

According to Wickman (1943), the migration energy depends on a number of factors, viz., the co-ordination, size, and charge of the ion, the degree of order in the structure, the temperature, and the pressure. The first three factors are the most important.

EFFECT OF CO-ORDINATION ON THE MIGRATION ENERGY

The ions possess a tendency to become arranged in the structure in a given co-ordination. The co-ordination number and the manner of co-ordination depend on the size and polarization of the ion and

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of the surrounding ions. In many structures, particularly in the rather complicated silicate minerals, the ions of a given element may occur in different co-ordinations, e.g., with reference to oxygen. Therefore, it follows that an ion in a given structure may have several different E -values. However, the ion prefers a certain co-ordination which is determined by its individual properties, principally by its size, and for this co-ordination the migration energy is greater than for any other possible co-ordination. The existence of several modifications of a mineral which have different structures but equal bulk composition illustrates the effect of co-ordination on the migration energy. The pair sillimanite-kyanite may be given as an example:

Mineral	Formula	Heat of Formation (kcal/mol)
Sillimanite...	$\text{Al}[\text{AlSiO}_3]$	623.7
Kyanite.....	$\text{Al}_2[\text{O} \text{SiO}_4]$	617.4

Kyanite is the unstable modification and tends to convert into sillimanite, which is stable under normal circumstances. The cause of the difference in stability is the difference in structure.

The mechanism of the incongruent melting of orthoclase may be explained, from an atomic standpoint, by applying the concept of migration energy. Orthoclase melts incongruently with the formation of leucite and a melt. The migration energy of the K^+ ion in the leucite structure differs from its migration energy in the orthoclase structure; in the former the migration energy evidently is higher. When orthoclase melts, the E -value of the K^+ ion in the orthoclase structure is reached, and all K^+ ions leave the disintegrating structure. The kinetic energy resulting from the oscillation of the ions now exceeds the migration energy of the K^+ ion in the orthoclase structure, but it is still lower than the migration energy of the K^+ ion in the leucite structure. Therefore, leucite remains stable, and only when the migration energy of K^+ in leucite is exceeded with increasing temperature will the fusion be accomplished.

EFFECT OF IONIC SIZE ON THE MIGRATION ENERGY

Because the co-ordination number of a cation surrounded by a co-ordinated polyhedron of anions is determined by the radius ratio of the ions, the size of cations with a given co-ordination number may vary only within certain limits which can be geometrically calculated for the different co-ordination numbers. If the ionic radius of the cation falls beyond the limits, another co-ordination is formed, and

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the co-ordination number of the cation changes. Consequently, the stability of co-ordination depends on ionic radius. A given co-ordination is at its most stable when the radius of the cation has an optimum value. Therefore, it is evident that the migration energy is greatest for a certain radius and smaller both for greater and for smaller radii because then the structure decreases in stability. For different cations with different radii but with similar charge and similar co-ordination in the structure, the migration energy is different and is a function of the radius.

The separation of forsterite, $\text{Mg}_2[\text{SiO}_4]$, from a crystallizing rock melt prior to fayalite, $\text{Fe}_2[\text{SiO}_4]$, may be understood by means of migration energy. Both Mg^{2+} and Fe^{2+} are 6-co-ordinated in these structures. The radius of Mg^{2+} (0.78 kX) is somewhat smaller than the radius of Fe^{2+} (0.83 kX). It was pointed out in an earlier paragraph that ferrous iron generally separates in a later stage of differentiation than magnesium does because its radius is greater and consequently the stability of structures containing ferrous iron is lower than that of structures containing magnesium. This is but a partial explanation. Evidently, the size of the Mg^{2+} ion is closer to the optimum size required by 6-co-ordination, and therefore the migration energy of Mg^{2+} in the olivine structure is greater than the migration energy of Fe^{2+} therein. The migration energy of the Be^{2+} ion with a radius of 0.34 kX is so small that beryllium is unable to form any stable structures in 6-co-ordination, and consequently no beryllium is able to enter into the olivine structure. Therefore, beryllium becomes enriched toward the later stages of crystallization. The structure of its orthosilicate phenakite, $\text{Be}_2[\text{SiO}_4]$, is entirely different from the olivine structure.

EFFECT OF IONIC CHARGE ON THE MIGRATION ENERGY

Of two cations with the same radius but with different charge, the cation with the higher charge must have the higher migration energy. The reason is that the cation with the higher charge is more strongly bound within the structure.

The crystallization sequence of the plagioclase feldspars may be explained by the differences between the magnitude of the migration energy of Ca^{2+} and that of Na^+ . The migration energy of Na^+ is lower than that of Ca^{2+} , and therefore the Na^+ ion is more mobile than the Ca^{2+} ion, especially at elevated temperatures. The result is that the calcic plagioclases separate at higher temperatures than do the sodic plagioclases.

With special reference to silicate minerals, it must be emphasized that the stability of the structure depends not only on the properties of the cations but also on the properties of the complex silicon-oxygen framework. The stability of minerals separated in the dark branch of the reaction series diminishes during the crystallization, showing that the stability of structures formed from chains of $[\text{SiO}_4]$ tetrahedra is lower than the stability of structures consisting of independent $[\text{SiO}_4]$ tetrahedra. However, the stability of a structure also depends on other factors, e.g., on the distance between the constituting particles, on their number in the unit cell, and on the nature of the bond. Many of the structural factors are still unknown, and consequently the crystal chemical discussion presented above will give only a rough and sketchy explanation of the course of crystallization.

DARK CONSTITUENTS

The occurrence of forsterite, the magnesium orthosilicate with independent $[\text{SiO}_4]$ tetrahedra in its structure, as the first-separated dark constituent is remarkable inasmuch as the separation of forsterite precedes the separation of enstatite, the magnesium metasilicate. The two minerals contain Mg^{2+} in 6-co-ordination. Therefore, it is evident that the properties of the Si-O framework will determine the order of crystallization of forsterite and enstatite. In the olivine structure the oxygen ions actually are packed more closely together than in the enstatite structure, and they resemble approximately a hexagonal closest packing.

In calc-alkalic rocks the calcium-free enstatite crystallizes prior to the calcium-bearing augite. Because the type of the silicon-oxygen framework is the same in all pyroxenes, the difference in their order of crystallization must be due to the presence or absence of calcium (and aluminum, alkali metals, etc.) in the structure. The radius of Ca^{2+} (1.06 kX) is considerably greater than the radius of Mg^{2+} (0.78 kX). If the large calcium ion enters the pyroxene structure, it will push the adjacent chains of $[\text{SiO}_4]$ tetrahedra farther apart, thereby decreasing the stability of the structure. This, of course, is only a rough explanation of the order of crystallization of the pyroxenes.

The averages calculated by Chirvinsky (1931) show that the composition of augite changes somewhat during the crystallization, as the content of magnesium decreases in relation to the content of calcium. This is illustrated in Table 5.34, which is calculated from the values presented in Table 5.22. It must be noted, in addition, that the aver-

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age iron content both in the orthorhombic pyroxenes and in the augites increases somewhat toward the later stages of crystallization.

The separation of the amphiboles after the pyroxenes may be explained by the differences in the silicon-oxygen framework. The structural differences between the pyroxenes and the amphiboles are shown in Figure 5.14 (see also Fig. 5.5). The double chains of $[\text{SiO}_4]$ tetrahedra in the amphiboles are somewhat looser and evidently less stable than the single chains in the pyroxenes. The co-ordination of the cations in the two groups of minerals is similar except that in the amphibole structure one of the five Mg^{2+} ions (or the replacing Fe^{2+} and other ions) is linked to only four O^{2-} ions. The remaining two bonds link it to two OH^- or F^- ions. The OH^- and F^- ions, however,

TABLE 5.34
CHANGES IN MOLECULAR $\text{MgO}:\text{CaO}$ RATIO IN AUGITE
SEPARATED DURING DIFFERENT STAGES OF
MAGMATIC CRYSTALLIZATION

	Augite from Pyroxenites, Lherzolites, Etc.	Augite from Gabbros and Norites	Augite from Augite Sye- nites and Augite Dio- rites
$\text{MgO}:\text{CaO} \dots \dots \dots$	1.91	1.18	0.92

do not belong to the double chains of the $[\text{SiO}_4]$ tetrahedra but occur as independent anions in the structure. The linkage differences of the Mg^{2+} ions evidently explain the order of crystallization of augite and hornblende.

The crystallization of micas after the crystallization of hornblende is explained by the fact that the structure of the micas is still weaker than the amphibole structure. Moreover, the K^+ ion is the most important cation in the micas, but, because of its low charge, it cannot be so strongly bound within the structure as can some other cations with higher charge in the same co-ordination.

LIGHT CONSTITUENTS

The atomic explanation of the crystallization of plagioclase feldspars was presented in an earlier paragraph. The plagioclase series is one of the best illustrations of the decisive effect of the properties of a cation, e.g., its charge, on the stability and energetic properties of a structure. Even though the silicon-oxygen framework of the plagioclases remains unchanged during the crystallization, the change in

the Na:Ca ratio is sufficient to maintain the separation of plagioclase from the early magmatic stage through the main stage of crystallization and still further.

ALKALIC ROCKS

The discussion of the crystallization sequence of the silicate minerals deals only with the normal calc-alkalic rocks. During the crys-

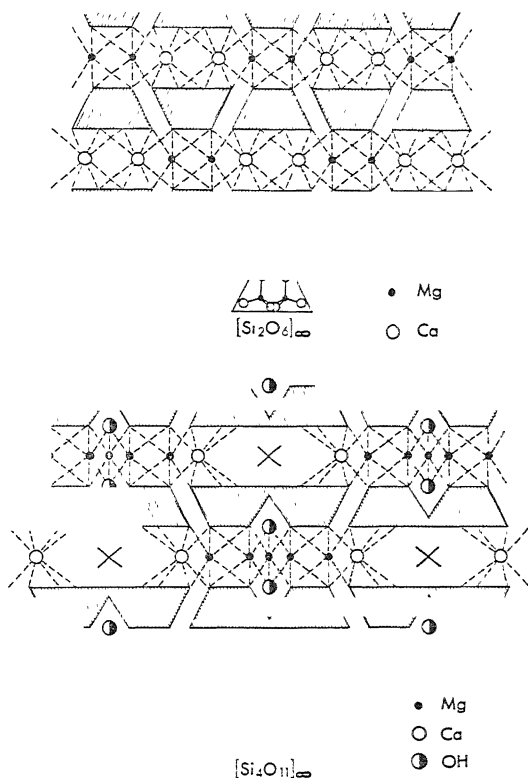


FIG. 5.14.—Schematic structure of the pyroxenes (*top*) and of the amphiboles (*bottom*). The *c*-axis is perpendicular to the plane of the paper. Alkali-metal ions may occupy the positions marked with a cross (X) in the amphibole structure.

tallization of the alkalic rocks the sequence of separation of the minerals may be entirely different, particularly when nepheline syenites are formed.

The formation of the basic, intermediate, and acidic calc-alkalic rocks usually starts with the separation of accessory minerals (ilmenite, magnetite, apatite, zircon, sphene), followed by the separation of augite, hornblende, and biotite, and of feldspars and quartz.

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In the alkalic rocks, in which both sodium and potassium predominate over aluminum, augite and hornblende are replaced by pyroxenes and amphiboles, in which sodium preponderates over potassium and ferric iron partly substitutes for aluminum outside the silicon-oxygen framework. The reason is that the sodium ion is smaller than the potassium ion and consequently is preferentially taken up by the pyroxene and amphibole structures. Because almost all aluminum is spent in the formation of feldspars and feldspathoids and because sodium preponderates among the alkali metals, $\text{Na}^+\text{-Fe}^{3+}$ silicates will form, which crystallize as pyroxenes and amphiboles. In alkalic rocks, augite is replaced by aegirite or aegirinaugite and hornblende by members of the riebeckite series. All gradations exist between aegirite and augite and between the riebeckites and the hornblendes.

With reference to energetic viewpoints, the alkali pyroxenes and alkali amphiboles may be compared to the plagioclase feldspars. The stability of the structure decreases from anorthite to albite. In a similar manner the stability decreases from augite to aegirite and from hornblende to arfvedsonite and riebeckite. The reason for the decrease is the increasing quantity of sodium as a constituent of the structure.

The stability of the pyroxene and amphibole structures is displayed by the crystallization sequence in nepheline syenites. Fersman (1929) divided the nepheline syenites according to their order of crystallization into two groups, viz., the miaskitic and the agpaitic nepheline syenites. The miaskitic group includes those nepheline syenites in which the crystallization sequence is analogous to the sequence in calc-alkalic rocks, that is, those in which the alkali pyroxenes and the alkali amphiboles separate prior to the alkali feldspars. In the agpaitic nepheline syenites the order is the reverse. The nepheline syenites of the Kola Peninsula in Russia belong to the agpaitic group. Their crystallization sequence is the following:

- (1) Nepheline
- (2) Alkali feldspars
- (3) Zirconium and titanium silicates
- (4) Na-Fe silicates (alkali pyroxenes and alkali amphiboles)
- (5) Volatile substances

The noteworthy content of sodium in the structures of the alkali pyroxenes and alkali amphiboles decreases their stability, and consequently they cannot separate before the alkali feldspars and nephe-

line do, and their materials remain in the residual melt. In the calc-alkalic rocks calcium causes the crystallization of the pyroxenes and amphiboles before the separation of the calcic plagioclases takes place, whereas in the alkalic rocks the light constituents are the first to separate. The normal crystallization sequence represented by the miaskitic types is probably the result of changes in the Na:Ca ratio and in the content of other cations in the plagioclase feldspars and in pyroxenes and amphiboles.

The differences in the sequence of crystallization of nepheline syenites are illustrated by the mineralogical composition of the nepheline syenite pegmatites. Pyroxenes and amphiboles do not occur in normal granite pegmatites, but aegirite and members of the riebeckite series are common constituents of the pegmatites of alkalic rocks. The agpaitic nepheline syenite pegmatites are usually characterized by an abundance of the dark constituents.

According to Fersman (1929), the miaskitic nepheline syenites, which are often rich in potassium, include the massifs of Serra de Monchique in Portugal, Ilmen Mountains in the Urals in Russia, Mariupol in the Ukrainian S.S.R., the Bancroft district in Ontario in Canada, and many others. The miaskitic nepheline syenites commonly occur on the boundaries of orogenic belts and often display vestiges of shearing stress. The two nepheline syenite massifs at Chibina and Lujaur Urt in the central part of the Kola Peninsula in Russia; the Ilmausak and other massifs in southern Greenland; those of Pilandsberg in Transvaal, Union of South Africa; Los Archipelago in the Atlantic Ocean; Magnet Cove in Arkansas in the United States; and Rio de Janeiro and Tingua in Brazil, among numerous others, belong to the group of the agpaitic nepheline syenites. The agpaitic types form huge massifs which usually show no sign of deformation. They occur as discordant injections in surrounding rock complexes. Some nepheline syenites are also known that occupy an intermediate position between the agpaitic and miaskitic types.

PEGMATITES

After the close of the main stage of crystallization there often remain residual solutions rich in hyperfusible constituents, especially in water, and the differentiation proceeds therein. The solutions commonly penetrate surrounding solidified rocks and form pegmatite veins and bodies. However, the pegmatitic liquors are not necessarily always left over from crystallization, inasmuch as the pegmatitic

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material may already have been consumed, directly or in reactions, during the preceding stage of crystallization. For example, in basic rocks albitization, chloritization, and other processes may be due to the action of residual liquors, and some granites also contain all their pegmatitic material. Pegmatites of granites and nepheline syenites—the last rocks to form during the main stage of crystallization—are rather common. Moreover, in the marginal parts or in the immediate neighborhood of massifs consisting of femic igneous rocks, such as gabbros, diabases, and pyroxenites, there often occur coarse-grained crystallates that differ chemically from the massifs and must be explained as pegmatites formed from the hydrous residual magmas. Pegmatites of acidic rocks are far more common than those belonging to intermediate and basic rocks because acidic rocks are more common than the basic ones and because, as a general rule, pegmatites are more acidic than the plutonic bodies from which they were derived (Landes, 1933).

The last crystallates formed during the pegmatitic stage of crystallization are called complex pegmatites. Hydrothermal replacement has taken place in the complex pegmatites, and rare minerals have been deposited in them. Therefore, they are important both mineralogically and geochemically. During the crystallization of a magma the elements having suitable ionic properties are removed by incorporation into the structures of rock-making minerals, whereas those elements for which this kind of removal is impossible and which are present in the melt in too small quantities to allow the formation of independent minerals become gradually enriched in the magmatic residue. Therefore, the pegmatites often contain, in high concentrations, a number of elements which are but rarely present in the early differentiates and in undifferentiated rocks. A number of heavy elements, such as thorium and uranium, become concentrated in the uppermost parts of the lithosphere because of their property of becoming enriched in granitic and pegmatitic melts of low density.

Elements which are particularly concentrated in pegmatites are, among others, lithium, beryllium, boron, fluorine, rubidium and cesium, the rare-earth metals, zirconium and hafnium, columbium and tantalum, and uranium. The elements typically enriched in pegmatites are listed in Table 5.35, according to Goldschmidt (1933*b*, 1934). This table comprises elements with very small ionic radius, which forbids their being camouflaged in the structures of common rock-making minerals. Beryllium and boron belong to this group;

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they are both elements typical of pegmatites. Another group among the elements typical of pegmatites contains those with too great ionic dimensions to allow them to replace diadochically the common constituents of rock-making minerals during the crystallization. Rubidium and cesium are examples of such elements. The ions of the rare-earth metals also are of dimensions great enough to cause a preferential enrichment of these elements in the pegmatites. During differentiation they become only partly trapped, e.g., in calcium

TABLE 5.35
ELEMENTS AND ELEMENT COMPLEXES TYPICAL OF AND ENRICHED IN
RESIDUAL LIQUORS OF SILICATE MAGMAS

Pegmatites	Pneumatolytic Deposits	Hydrothermal Deposits
<i>Li</i> (Cs)	<i>Li</i>	Ag Au
Be (Mn)	Cu	Ba (Sr) Mn Zn Pb Cu
Sc B Y La TR	Sc B As	(B) As Sb Bi
Ti Zr Hf Th Ce	Sn	
Cb Ta (P)	(Ta) P	
Mo (W) U	Mo W	(Mo) U
F Cl OH CO ₂	F Cl OH CO ₂	F Cl OH CO ₂
(S)	S	S Se Te

minerals. Because of energetic reasons the Li^+ - Mg^{2+} diadochy removes only a part of lithium into rocks formed during the main stage of crystallization.

Rather pronounced differences exist in the distribution of a number of rare elements in granite pegmatites and in nepheline syenite pegmatites. Uranium, columbium, tantalum, scandium, yttrium, and the weakly basic yttrium-earth metals are predominantly concentrated in granite pegmatites, whereas the strongly basic cerium-earth metals, zirconium, and often thorium are enriched in the nepheline syenite pegmatites. Moreover, the zirconium minerals of granite pegmatites are richer in hafnium than are the zirconium minerals of nepheline syenite pegmatites. Further, the Fe^{3+} and Ce^{4+} ions seem

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to occur preferentially in the nepheline syenite pegmatites, whereas Fe²⁺ and Ce³⁺ minerals are characteristic of the granite pegmatites. The elements enriched in the most important groups of pegmatites of acidic rocks, i.e., in granite and nepheline syenite pegmatites, are presented in Table 5.36, according to Goldschmidt (1930*c*, 1933*b*).

Geochemical concealing and the enrichment of certain elements in pegmatites prove that the ionic dimensions may often decisively affect the manner of occurrence of elements in rocks. However, the size of an ion does not always predict its geochemical behavior in igneous rocks, and, in spite of its importance, the ionic radius is not the sole factor in determining the distribution of an element in igneous sur-

TABLE 5.36
ELEMENTS CONCENTRATED IN GRANITE PEGMATITES AND
IN NEPHELINE SYENITE PEGMATITES

Granite Pegmatites											Nepheline Syenite Pegmatites										
Li											(Li)										
Be											Be										
B											B										
Sc	Y	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		La	Ce	Pr	Nd	Sm	Eu					
La	Ce	Pr	Nd	Sm	Eu						Y	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Ti	Zr	Hf	Th								Ti	Zr	Hf	Th							
Cb	Ta	P									Cb	(Ta)	P								
Mo	(W)	U									(Mo)	(U)									
F	(Cl)										Cl	F									
(CO ₂)											CO ₂										

roundings. Columbium and tantalum are examples of elements whose behavior is not determined merely by ionic size. They are chemically closely related and consequently nearly always accompany each other in minerals and in other natural surroundings. The radii of quinquivalent columbium and tantalum are nearly identical with the radius of ferric iron, and therefore one would expect the two metals to be enriched in iron minerals, by substituting ferric iron therein. However, columbium and tantalum, often in the form of independent minerals, are typical constituents of pegmatites (see chap. 26).

The enrichment of many otherwise rare constituents of rocks in the pegmatites is responsible for the fact that pegmatites often contain a wealth of independent minerals of rare elements not found elsewhere. Some of these minerals are used as ores of rare elements. According to their bulk chemical composition, the pegmatites may be divided into two groups (Goldschmidt, 1930*c*). The first group comprises the agpaitic pegmatites. They belong to the differentiation products of agpaitic magmas, and in them the atomic abundance of

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sodium and potassium is higher than the atomic abundance of aluminum:

$$\text{Na} + \text{K} > \text{Al}.$$

In the second group, the plumasitic pegmatites, aluminum predominates over sodium and potassium:

$$\text{Na} + \text{K} < \text{Al}.$$

Lithium is not considered with sodium and potassium in the geochemical classification of the pegmatites because it does not form a

TABLE 5.37
TYPICAL MINERALS OF AGPAITIC AND
PLUMASITIC PEGMATITES

Agpaitic Minerals	Plumasitic Minerals
Aegirite	
Riebeckite	
Arfvedsonite	
	Dumortierite
	Cordierite
	Corundum
	Topaz
Catapleite	
Eudialite	
Eucolite	
Elpidite	
Leucophane	Beryl
Meliphanite	Chrysoberyl
Epididymite	
Eudidymite	
Homilite	Tourmaline
Cappelenite	
Mosandrite	Allanite (Orthite)
Steenstrupine	
Lepidomelane	Muscovite
Astrophyllite	
Epistolite	Euxenite
Wöhlerite	Columbite

feldspar. The agpaitic character of a pegmatite is proved, e.g., by the occurrence of minerals in which the excess of sodium and potassium accompanies iron, as in aegirite, $\text{NaFe}[\text{Si}_2\text{O}_6]$, whereas the plumasitic pegmatites may contain minerals like corundum, $\alpha\text{-Al}_2\text{O}_3$. Some typical minerals of the agpaitic and plumasitic pegmatites are presented in Table 5.37, according to Goldschmidt (1930*c*, 1933*b*).

Along with the minerals listed in Table 5.37 a number of "neutral" minerals occur in the pegmatites, e.g., the alkali feldspars, nepheline, and leucite, in which $\text{Na} + \text{K} = \text{Al}$. Quartz and zircon are also neutral minerals, whereas calcic plagioclase is a typically plumasitic mineral.

The pre-Cambrian granite pegmatites of southern Norway and the

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spodumene-bearing granite pegmatites of the Black Hills in South Dakota in the United States are well-known representatives of plumbasic pegmatites. The pegmatites of southern Greenland and those of the central parts of the Kola Peninsula in Russia, among others, belong to the group of agpaitic pegmatites.

Many ore minerals are also present in the pegmatites. Native gold and platinum occur in some pegmatites, and cassiterite, wolframite, and magnetite are abundant in many. Among the sulfide minerals, only molybdenite is more consistently found in pegmatites. Other sulfide minerals present are pyrite, arsenopyrite, bornite, chalcopyrite, galena, and sphalerite. The ore minerals occurring in pegmatites, according to Landes (1937), have been precipitated from hydrothermal solutions which merge into the pegmatites. Tin, tungsten, and molybdenum are connected with granite pegmatites and associated hydrothermal veins, whereas gold and sulfide minerals are found in pegmatites and hydrothermal deposits produced from intermediate magmas.

The previous discussion refers to the complex pegmatites. There is, in addition, another group of pegmatites called simple pegmatites. They do not represent any specific products of crystallization, and no hydrothermal replacement has taken place in them. They are formed in paligenetic processes by the remelting of rocks. The simple pegmatites resemble the complex ones externally because they form very coarse-grained veins and bodies. However, they are mineralogically and geochemically entirely different from the complex pegmatites. They do not contain noteworthy concentrations of rare elements and rare minerals but rather correspond, chemically, to the last products formed during the main stage of magmatic crystallization.

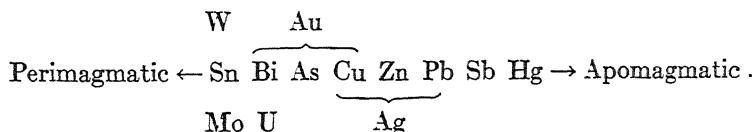
PNEUMATOLYTIC AND HYDROTHERMAL DEPOSITS

The formation of pegmatites still belongs to the magmatic stage of crystallization. The pegmatites separate from a residual melt containing much water and other mineralizers, e.g., acid vapors. Materials crystallizing as silicates, however, form the bulk of the melt. The formation of pegmatites marks the end of the magmatic crystallization in the strict sense of the term. No sharp boundary can be established between the pegmatitic stage and the ensuing pneumatolytic and hydrothermal stages during a notably fractional crystallization, but it is customary to treat the pneumatolytic and hydrothermal formations separately from the pegmatites. When a superheated

aqueous solution containing dissolved silicates and other substances crystallizes above the critical temperature of water vapor ($374^{\circ}5$ C.), the deposits formed are called pneumatolytic. If the crystallization takes place at a temperature below the critical temperature of water vapor, the resulting rocks and minerals are called hydrothermal.

The chief minerals formed during the pegmatitic stage are silicates, mainly alkali feldspars and micas, quartz, and the characteristic minerals containing rare elements. The mineral veins are the most important among pneumatolytic and hydrothermal deposits. Many heavy metals are separated in such veins and may form ore bodies of high economic importance. The vein deposits contain many sulphophile metals either in the native state or as oxides, sulfides, arsenides, antimonides, selenides, tellurides, and various sulfosalts. Almost all metals found in the vertical subgroups of the Periodic System occur in the metalliferous veins. The elements typical of pneumatolytic and hydrothermal deposits are presented in Table 5.35.

The hydrothermal deposits are commonly classified according to their temperature of formation. With decreasing temperature, the order of the hydrothermal deposits formed is the following: perimagmatic, apomagmatic, cryptomagmatic, and telemagmatic. The perimagmatic deposits, formed at the highest temperatures, have remained close to the intrusive center. The materials of the apomagmatic minerals may have migrated farther into the surrounding rocks, whereas the cryptomagmatic and, in particular, the telemagmatic materials, because of their low temperature of crystallization, have migrated too far from their igneous home to allow a definite identification of their source. The heavy metals found in the mineral veins may form independent minerals over a wide range of temperatures. It follows that, in general, each metal tends to form a zone around the intrusive center. However, the zones are not strictly defined, and the zonal arrangement is far from ideal. At any rate, the following order of separation may be given for some of the metals in question (Berg, 1929):



Iron and sulfur are present in all zones. The zone of tellurium coincides closely with the zone of gold, and the zone of selenium with that of silver.

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It is believed that the pneumatolytic and hydrothermal emanations are first acid in reaction, owing to the presence of HCl, HF, H₂S, H₂SO₄, H₂CO₃, H₃BO₃, and other volatile acids. In reactions with surrounding rocks they are neutralized, and in a later stage the solutions may be alkaline because of the presence of alkali salts of weak acids, such as alkali carbonates, borates, and sulfides. Unless they are completely consumed in mineral-producing reactions, the alkaline solutions, mixed with meteoric waters, reach the surface in hot springs. Sometimes, when the intrusive mass lies at a shallow depth, even acid emanations, such as vapors or acid waters, may be encountered on the Earth's surface.

After deposition of most of their metallic constituents, the water-rich hydrothermal residual solutions may deposit quartz, zeolites, and, if other volatile constituents are present, such minerals as datolite, Ca[OH|BSiO₄], and thaumasite, Ca₃H₂[CO₃|SO₄|SiO₄]·14H₂O. The abundant formation of zeolites probably requires addition of water from extraneous sources. The late hydrothermal solutions may merge with surface waters, and consequently hydrothermal processes and secondary changes during the weathering often become indistinguishable.

VOLCANIC EMANATIONS

During magmatic differentiation the most readily volatile constituents become concentrated in pneumatolytic and hydrothermal deposits. Little is known of the concentration of the volatiles in a melt or in its derivatives until they rise to the Earth's surface along cracks and fissures surrounding the magma basin. In volcanoes the magmas reach the surface, and their volatile constituents, as volcanic emanations, escape into the atmosphere, dissolve in water, and form sublimates around the craters and vents. On the bottom of the ocean, volcanic springs produce emanations that dissolve in sea water.

A typical analysis of volcanic emanations is presented in Table 5.38, according to Graton (1945). The analysis is based on E. S. Shepherd's selection of the most reliable analyses of gases from the active Halemaumau lava lake in Hawaii. The analysis shows that water vapor is the most important component of the emanations. It is followed by carbon dioxide, nitrogen, and native and combined sulfur. The analysis of Table 5.38 represents the composition of the gases after the deduction of all oxygen and of the normal atmospheric proportion of nitrogen, carbon dioxide, and argon, because the gas samples were contaminated by surface air.

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The composition of volcanic gases shows notable local and areal changes, some of which are attributed to the composition of the individual magmas. However, the surrounding rocks noticeably affect the composition of the ascending gases because the gases react with the rocks under precipitation of some of their constituents and under uptake of new volatile compounds. Therefore, it follows that all the constituents of volcanic emanations do not necessarily derive from the magma (juvenile constituents) but may partly become incorporated from the Earth's surface (superficial constituents) or from the atmosphere (meteoric constituents).

TABLE 5.38
AVERAGE CHEMICAL COMPOSITION OF
HALEMAUMAU GASES

CONSTITUENT	PER CENT	
	By Volume	By Weight
H ₂ O..	67 68	45 12
CO ₂	12 71	20 71
SO ₂	7 03	16.67
N ₂	7 65	7.93
SO ₃	1 86	5.51
S ₂	1.04	2 47
CO..	0 67	0 69
Cl ₂	0 41	0.54
A...	0 20	0.30
H ₂	0 75	0.06
Total...	100 00	100 00

Ch. Sainte-Claire Deville and F. Leblanc concluded, in 1858, on the basis of numerous analyses of fumarole gases from Mediterranean volcanoes, that the composition of the emanations varies with the time elapsed since the start of the volcanic activity and with the distance of the vents from the center of activity. The temperature of the emanations affects their chemical composition, and their temperature, again, depends on the length of the path from the center of activity through the much cooler rocks to the vent.

The gases separating at elevated temperatures are rather dry. They contain superheated water vapor, relatively much free hydrogen, carbon monoxide, methane, metal chloride vapors, and gaseous fluorides. According to the theory, free oxygen, sometimes present in the high-temperature emanations, does not belong to the uncontaminated emanations. With decreasing temperature, hydrogen and car-

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bon monoxide start to oxidize to water and carbon dioxide, respectively, and sulfur is partly oxidized to dioxide. Water vapor reacts with the chlorides under the production of hydrochloric acid. The acid vapors may react with the surrounding rocks. They release hydrogen sulfide from sulfide minerals and carbon dioxide from carbonates. Consequently, they gradually become exhausted, and water vapor, carbon dioxide, and indifferent gases, e.g., nitrogen, are the main constituents of the emanations when the volcanic activity has decreased much in intensity. Finally, carbon dioxide also disappears, and only water vapor is given off.

TABLE 5.39
AVERAGE COMPOSITION OF FUMAROLIC GASES
OF KATMAI REGION

Constituent	Per Cent by Volume
H ₂ O (water vapor).....	99.65
<i>Fixed gases:</i>	
CO ₂	0.097
O ₂	0.002
CO.....	present
CH ₄	0.015
H ₂ S+H ₂	0.024
N ₂ +A.....	0.041
Total of fixed gases.....	0.179
<i>Soluble gases:</i>	
H ₂ S.....	0.029
HCl.....	0.117
HF.....	0.032
Total of soluble gases....	0.178
Grand total	100.007

Allen and Zies (1923) analyzed the gases from the fumaroles of the Katmai region in Alaska. The average composition of the gases is presented in Table 5.39. The principal gases other than water vapor are hydrochloric acid, carbon dioxide, nitrogen, hydrofluoric acid, hydrogen sulfide, and sometimes also methane. Minor gaseous constituents are oxygen, carbon monoxide, argon, and ammonia (generally as chloride and probably as fluoride). Water vapor and the inert gases in the Katmai fumaroles are believed to be chiefly of surface origin, owing to the admixture of meteoric waters with those of juvenile origin in the uppermost parts of the volcanic channels.

Geochemically, the volcanic emanations are of high importance. Their total quantity on the Earth cannot be directly estimated be-

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cause the data available are insufficient. However, a reasonable estimate may be made on the basis of the content of the elements of the emanations in sedimentary rocks, in the atmosphere, and in the hydrosphere. Goldschmidt's (1937*b*) estimate of the amount of the products of degassing is presented in Table 5.40.

It is believed that several volatile substances, in particular the chlorides of Na, K, Fe, Al, Zn, Cu, Pb, and other metals, are important constituents of the emanations. Fluorides seem to be somewhat less important. The chlorides of sodium, potassium, ammonium, and ferric iron probably are the most common and most abundant vol-

TABLE 5.40
AMOUNT OF PRODUCTS OF DEGASSING ON THE EARTH

Element	Amount on the Earth ($g \cdot cm^{-2}$)	Atoms per 100 Atoms of Hydrogen
H.....	31,000	100
B.....	26	0.008
C.....	2,300	0.6
N.....	770	0.18
O*.....	253,000	51
S.....	475	0.046
Cl.....	5,365	0.5
Se.....	0.1	0.000004
Br.....	18	0.0007
I.....	0.09	0.000002

* As H_2O and CO_2 .

canic sublimates. Silicofluorides and alkali carbonates also are of considerable abundance, and sulfates of the alkali metals, like glaserite (apthitalite), $NaK_3[SO_4]_2$, have also been met in the sublimates. Alkali chlorides are abundant in hot-spring waters. E. T. Allen (according to Fenner, 1933) found that the amount of chlorine (as chlorides) discharged in the waters from the Norris Geyser Basin in the Yellowstone National Park in Wyoming in the United States may reach nearly 3,200 kg per day.

Iron as ferric chloride, hematite, pyrite, or pyrrhotite is often connected with fumarolic activity. The heavy metals occur in the fumarolic incrustations as oxides, chlorides, oxychlorides, hydrated chlorides, and carbonates. Some metals may be characteristic of certain volcanic areas. Thus copper is considered to characterize the fumaroles of Etna and lead those of Vesuvius, even though the two metals are found in the fumaroles of both areas.

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The following elements are reported in the fumarole deposits of the volcano Stromboli in the Tyrrhenian Sea:

Fe (abundant hematite, α -Fe₂O₃; magnesioferrite, MgFe₂O₄;
soluble compounds)
S, Se, Te
Li, Tl (sulfates)
I
P
Zn, Sn, Pb, Bi, Cu (soluble compounds)
B (boric acid)
N (sal ammoniac)
As (realgar; soluble compounds)
K, Rb, Cs (alums)
Na (mirabilite, Na₂[SO₄]·10H₂O; glauberite, Na₂Ca[SO₄]₂)
Ca (glauberite)

Zies (1924) presented evidence on the concentration of elements in volcanic areas through vapor-phase activity and through the solvent action of acid or alkaline aqueous solutions. He reported the presence of heavy metals in many fumarolic deposits collected, in 1919, in the Valley of Ten Thousand Smokes in Alaska. Here the volcanic activity is caused by the intrusion of rhyolite under the valley floor. Lead, zinc, and tin were found in nearly all incrustations of the vigorously active fumaroles. The interaction of the acid gases and other volatile compounds, such as HCl, HF, H₂S, SO₂, S, and NH₄ salts, released by the fumarolic activity, with the extruded pumice produced a notable mineralization in the pumice. The fluorine content ran as high as 3.8 per cent. Several tons of well-crystallized fumarolic magnetite, evidently produced in the reaction between iron halogenide vapor and water vapor, were visible in a series of fissure vents. The magnetite was analyzed chemically and spectrochemically for its minor constituents. The analysis is presented in Table 5.41.

According to Zies (1938), the analysis of other incrustations revealed the presence of Bi, Ga, Tl, B, Ge, As, Se, and Te. Molybdenum was often present as the hydrated oxide ilsemanite (molybdenum blue), which colored areas covering several thousand square meters.

In 1923 the temperature and general activity of the fumaroles had decreased to a point where the condensation of water vapor took place. The acid gases were in solution, all the magnetite was decomposed, and in its place covellite, CuS; chalcocite, Cu₂S; galena, PbS; pyrite, FeS₂; and sphalerite, ZnS, were found, along with cotunnite, PbCl₂, and hematite, α -Fe₂O₃. Ammonium chloride, sulfur, borates, and fluorides had also been deposited.

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The volcanic emanations affect essentially the manner of occurrence and the geochemical cycle of many elements. Thus, for example, chlorine, sulfur, and boron, which, according to Table 5.40, are plentiful in volcanic emanations, are thereby added to the minor cycle. Volcanic emanations must be considered an important source of many elements participating in geochemical phenomena on the Earth's surface. This is illustrated by the estimates of Zies (1938) on the total amount of the acid gases released, in 1919, by the fumaroles in the Valley of Ten Thousand Smokes:

Compound	Tons
HCl... ..	$1.3 \cdot 10^6$
HF... ..	$0.2 \cdot 10^6$
H ₂ S... ..	$0.3 \cdot 10^6$

TABLE 5.41
MINOR CONSTITUENTS OF FUMAROLIC MAGNETITE FROM THE VALLEY OF TEN THOUSAND SMOOKES IN ALASKA

Constituent	Per Cent by Weight
Zn	0.47
Cu	0.23
Mo	0.04
Co	0.02
Ni	0.01
Pb	0.005
Sn	~0.004
MnO	0.13
TiO ₂	0.005
Sb	present
Hg, V, Cr, As, Bi	absent
S	0.27
NaCl	0.05
Siliceous residue	0.53

Even though a part of the emanations is of surface origin, the importance of volcanic emanations in affecting the geochemical balance of many elements cannot be overestimated.

THE MINOR CYCLE AND ITS PRODUCTS

THE EXOGENIC CYCLE OF MATTER

The upper lithosphere is the seat of numerous geochemical processes. Both local and areal changes in its chemical composition have taken place during the geological evolution of the Earth. All matter on the Earth's surface and in the uppermost layers of the lithosphere participates in a slow, but rather complicated, migration. This migration of matter, or its cycle, causes more or less pronounced dis-

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turbances or a total change in the structure and chemical composition of rocks, and new rocks with new properties represent the result thereof.

The migration of matter may be divided into two parts: the minor (or exogenic) cycle and the major cycle. The minor cycle takes place under the direct influence of hydrospheric and atmospheric agents,

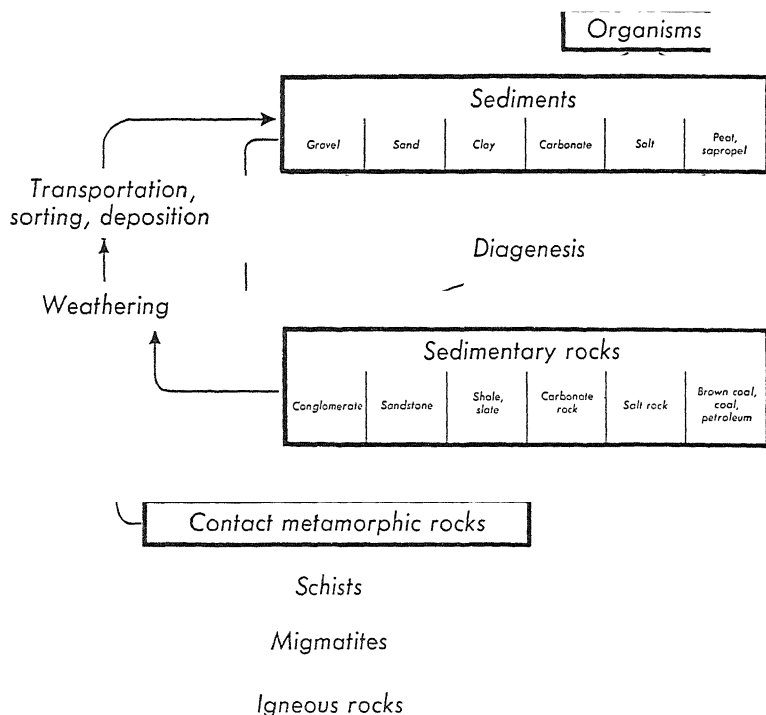


FIG. 5.15.—The minor cycle

whereas a material part of the major cycle is confined to the uppermost levels within the lithosphere.

In the chemical reactions taking place during the exogenic cycle the elements behave differently, according to their individual properties. The phenomena and laws connected with the exogenic cycle differ basically from the rules valid for the crystallization of magmas. Consequently, the migration of the elements is governed, at least partially, by different principles and results in the formation of products whose existence cannot be explained on the basis of observations on magmatic crystallization. Geochemically, it is very important to

survey the distribution of the elements in products of the minor cycle.

The minor cycle starts from solid crystalline rocks and ends in sedimentary rocks. It forms but a part of the major cycle of matter in Nature, and, unlike the major cycle, which is closed, it is largely open and takes place only in one direction. The minor cycle is closed only for sedimentary rocks, but for other rocks it is irreversible. The minor cycle is of high importance for the manner of occurrence of the elements in the uppermost lithosphere. This is due to its role as a separating and concentrating agent for a number of elements.

The course of the exogenic cycle of matter is schematically presented in Figure 5.15. It consists of the weathering of rocks, the transportation of products formed in weathering, and the redeposition of the materials, usually in new surroundings. These processes are in many respects similar to a gigantic semiquantitative chemical analysis, carried out by Nature and involving chemical separations on a large scale.

FORMATION OF SEDIMENTS

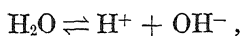
WEATHERING

The first stage of the minor cycle is the decomposition or weathering of rocks. Rocks belonging to all the three main classes—igneous rocks, sedimentary rocks, and metamorphic rocks—participate in this process. Weathering consists of a number of processes that gradually break down the fresh solid rocks into an aggregate of loose material, some of which goes into solution, while another part succumbs to chemical changes and still another part remains unchanged in composition. The decomposing agents are either physical (mechanical) or chemical. The chief mechanical agents are changes of temperature and the action of frost and crystallizing salts. They only break down the rock into separate particles, which are more likely to succumb to chemical reactions. Consequently, the mechanical processes may be considered to form the first step of decomposition by furnishing fresh mineral surfaces for the subsequent more powerful chemical attack.

Chemical decomposition is caused by the action of rain, surface, and ground water and of the solids and gases dissolved therein. The presence of water is the basic requirement of all chemical weathering. It is known that ultimately all minerals are soluble in water. Rain water falling on the surface of a rock and flowing over it dissolves the

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rock minerals or decomposes them chemically. The action of water depends rather strongly on its pH. Pure water with pH 7 possesses a rather weak decomposing action, whereas both acid and alkaline solutions decompose minerals at a rate which is proportional to the difference between the pH of the solution and the pH of pure water. Oxygen, carbon dioxide, nitric acid, sulfuric acid, humic complexes, ammonia, and chlorides are the most important among the decomposition-promoting substances dissolved in natural waters. Also the action of organisms promotes the decomposition of rocks. Because pure water, which contains no dissolved substances, is slightly dissociated according to the equation



the dissociated part thereof is chemically more active as a decomposing agent than is the undissociated part.

The substances dissolved in water come from the atmosphere (chiefly oxygen, carbon dioxide, nitrates, and chlorides), from previously weathered rocks (carbon dioxide and carbonates, sulfuric acid and sulfates, chlorides), from the decaying remains of organisms (nitric acid, nitrates, ammonia, carbon dioxide, humic complexes), and from volcanic emanations.

The chemical processes taking place in weathering are rather complicated. They include hydration and hydrolysis, oxidation and reduction, action of carbon dioxide (carbonation), and solution.

In hydration, water is adsorbed on the surface of the mineral grains. The combination with water, as in the formation of gypsum from anhydrite, also belongs to this group. Often the first uptake of water is not connected with changes in the mineral structures, but finally the materials go into solution as ions or colloidal particles. Hydrolysis is closely associated with hydration. It was previously held that hydrolysis is the most important process in decomposition, but Correns and von Engelhardt (1939) showed that both acid and alkaline solutions possess a more strongly decomposing action than do neutral solutions. Therefore, the action of acids and bases in the weathering of silicate minerals is more important than hydrolytic decomposition is.

Both inorganic and organic substances may cause oxidation. The organic oxidation is chiefly the result of bacterial decomposition and of respiration of higher organisms. The oxidation during weathering affects the cycle of many elements, e.g. carbon, nitrogen, phosphorus,

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iron, and manganese. Moreover, the oxidation of sulfur compounds, e.g., of sulfide minerals, is geochemically highly important because sulfuric acid, which may form as an oxidation product, is a powerful decomposing agent and therefore promotes further weathering.

Along with oxidation, numerous other chemical processes take place in the zone of weathering. They are chiefly connected with the biological activity of plants and micro-organisms, e.g., photosynthesis, putrefaction, and the action of sulfate- and nitrate-reducing bacteria. Some of these processes are discussed in chapter 8 and in Part II of this book. Among the inorganic processes, those active in the zone of reduction of ore deposits and the reduction of sulfur to hydrogen sulfide, along with a number of others, are of geochemical importance.

TABLE 5.42
ORDER OF RATE OF LOSS OF CHEMICAL CONSTITUENTS
DURING WEATHERING, ASSUMING
ALUMINA CONSTANT

Gneiss	Diabase	Amphibolite
Na ₂ O	CaO	CaO
CaO	MgO	Na ₂ O
MgO	K ₂ O	MgO
K ₂ O	Na ₂ O	Fe
SiO ₂	SiO ₂	SiO ₂
Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃
Fe (gain)	Fe (gain)	K ₂ O (gain)
H ₂ O (gain)	H ₂ O (gain)	H ₂ O (gain)

The role of carbon dioxide in weathering is very important. The increased effectivity of carbon dioxide-bearing waters, as compared with pure water, in attacking silicate minerals has been proved by experiment. According to Goldich (1938), the role of carbon dioxide may be chiefly in the reduction of alkalinity during the hydrolysis rather than in direct chemical action, but the results of Correns and von Engelhardt (1939) would seem to contradict this conclusion.

During prolonged weathering all constituents of the minerals are ultimately lost, with the exception of water. The rate of loss depends on a number of factors, among which the composition of the rock and the climate are the most important. Goldich (1938) has given the order of the rate of loss of important constituents for three rocks in which the decomposition was found to be significant (Table 5.42). Goldich's table and similar results obtained by other investigators show that the weathering processes operate with rather high uniformity.

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The rock-making minerals possess different degrees of stability against weathering. Thus, e.g., the rate of decomposition of olivine exceeds that of pyroxene in a normal igneous rock, and the mafic minerals decompose at a more rapid rate than do the felsic minerals. Goldich (1938) arranged the common rock-making minerals in two series according to increasing stability. This arrangement is shown in Figure 5.16, which illustrates the stability principle. Hypersthene is added, according to Pettijohn (1941). The arrangement actually is the same as Bowen's reaction series (see under "Chemical Differentiation of Igneous Rocks," p. 157). The reaction series indicates the

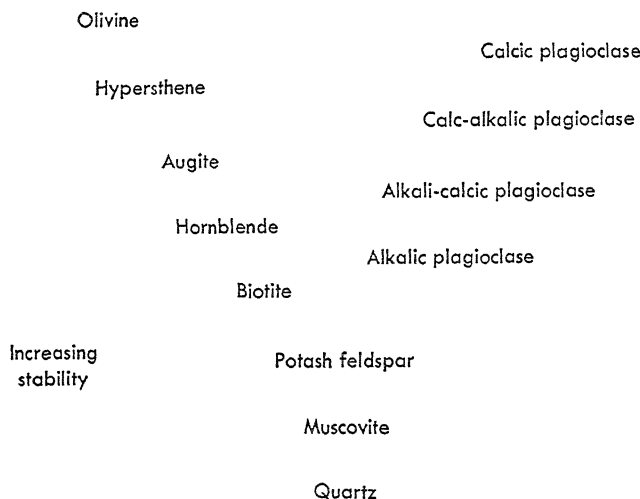


FIG. 5.16.—Stability of minerals in weathering

stability of minerals during their crystallization from a melt, whereas Goldich's series indicates their susceptibility to weathering. Minerals crystallized at the highest temperatures from the most anhydrous magmas are less stable against weathering under the conditions met on the Earth's surface than are the minerals formed at low temperatures from the water-rich residual melts. According to Goldich (1938), the differential between the equilibrium conditions at the time of formation and those existing on the Earth's surface during decomposition may, perhaps, govern the order of stability of the minerals.

Pettijohn (1941) expanded Goldich's stability series to a number of common constituents of sediments. The complexity of the heavy-mineral suites of arenaceous sediments increases with decrease in age

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because the less stable species disappear by intra-stratal solution in the older deposits. The order of persistence found by Pettijohn is shown in Table 5.43. However, as Reiche (1945) points out, the equivalence of persistence and resistance to weathering is not demonstrated, even though the two phenomena, in general, must be closely related.

TABLE 5.43
ORDER OF PERSISTENCE OF MINERALS
FOUND IN ARENACEOUS SEDIMENTS

Increasing tendency of formation	↑	Anatase Muscovite Rutile
<hr style="border-top: 1px dashed black;"/>		
Increasing tendency of destruction	↓	Zircon Tourmaline Monazite (Quartz) Garnet Biotite Apatite Ilmenite Magnetite (Feldspar) Staurolite Kyanite Epidote Hornblende Andalusite Topaz Sphene Zoisite Augite Sillimanite Hypersthene Diopside Actinolite Olivine

The solid products of completed weathering include materials which are stable under the conditions existing on the Earth's surface. Clay minerals, the hydroxides of ferric iron and aluminum, and their derivatives are the most abundant weathering products. However, the clay minerals may become decomposed, whereby sesquioxides of iron and aluminum are finally produced.

SEDIMENTATION

During chemical decomposition the rock minerals either go into ionic or colloidal solution or remain *in situ* in the form of weathering residues and of insoluble hydrolytic residues. The loose weathering

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residues are transported and sorted by the action of wind, flowing water, ice, and organisms. Moreover, gravity and changes in temperature may cause transportation. The result of the transportation and sorting of weathered materials is the formation of a number of chemically and physically different continental and marine sediments, such as gravel, sand, clay, calcareous mud, flocculated colloidal ferric hydroxide, and precipitated water-soluble salts. Thick beds of these and other materials may become deposited in suitable environments, the most important of which are the basins of the seas and oceans.

During the transportation the materials generally become sorted according to their particle size. The sorting also includes chemical separation. The coarse-grained particles with particle size in excess of 2 mm still mostly contain chemically unaffected rock and mineral material, i.e., mixtures of various elements. Quartz is a common and essential constituent in the fractions of grains with a diameter of 2–0.02 mm. Concentration of silicon may consequently take place by a purely mechanical accumulation of the silica-rich fractions. The proportion of the newly formed aluminum silicates (see under “Hydrolyzates,” p. 202) increases parallel with the decrease in particle size, and consequently the accumulation of pure clays is possible and leads to a concentration of aluminum.

FORMATION OF SEDIMENTARY ROCKS

DIAGENESIS

In the course of time changes may occur in the deposited loose sediments. They lead to the consolidation and recrystallization of the beds by diagenesis. Solutions circulate in pores between the mineral particles and in cracks and deposit various materials in the empty spaces. The particles are bound together, and the loose sediment is converted into a coherent solid mass. Thus a sedimentary rock is formed.

The diagenetic changes start as soon as the sediment is deposited. Compaction, solution, recrystallization, replacements, formation of new minerals, and cementation take place in the sediments during diagenesis. Some of the diagenetic changes are expulsion of water, reduction of ferric to ferrous iron, formation of iron sulfides, and oxidation of organic matter. Calcium carbonate may become dolomitized, and silica may precipitate from circulating solutions. Aragonite converts into calcite, and gypsum is dehydrated or anhydrite is hy-

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drated. In general, the mechanism and the causes of these and numerous other diagenetic changes are still very inadequately understood.

Diagenetic changes are promoted by increase in temperature, which may be the result of the neighborhood of a hot magma mass, as in volcanic regions, radioactive decay, or the sinking of the material into the deeper layers of the uppermost lithosphere, owing to the weight of the superimposed beds. Increasing pressure also promotes diagenesis. Thus in diagenesis conglomerates are formed from gravel, sandstones from sand, shales and slates from clay, etc.

Actually, all intermediate stages leading from diagenesis to metamorphism are present, and no material difference exists between the two processes. Temperatures and pressures that do not bring about the solidification of sand and of calcareous mud produce typical metamorphic changes in salt deposits. Diagenesis includes changes in chemical composition, often due to the presence of organisms or their remains in the sediments. Changes in temperature and pressure may produce changes in solubility of the constituents of the sediments. The net result is recrystallization and cementation, combined with the migration of matter in an intergranular ionic diffusion or due to solution in interstitial liquids by which colloids may also be transported.

A number of sediments and their derivatives also form from the remains of organisms. Calcareous mud and ooze, peat, and guano, among others, belong to this group of sediments. Calcitic and dolomitic limestones, brown coal, coal, petroleum, phosphorite, and other rocks are formed from these sediments through diagenesis or decay and incoaling.

GEOCHEMICAL CLASSIFICATION OF SEDIMENTS AND OF THEIR DERIVATIVES

A part of the products from the decomposition of rocks consists of solid particles which are transported to the loci of sedimentation or are deposited in the original seat of decomposition. Another part is present in solution either as ions or as colloidal particles and remains dissolved until a separation in proper surroundings takes place. Therefore, sediments often are divided into two classes, viz., sediments of physical (mechanical) deposition or physical (mechanical) sediments and sediments of chemical deposition or chemical sediments. Even though this classification is based on the manner of for-

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mation of the sediments and may be used to characterize the sediments according to viewpoints pertaining to their texture and composition, it is geochemically inadequate. It must be noticed that the weathering products classified as physical sediments contain, along with chemically undecomposed material that occurs as relics in the sediment, substances that no longer represent the mineral structures from which they were produced during the decomposition. The new materials are often already formed in the original locus of decomposition. They, of course, differ chemically from the undecomposed weathering residues. In a similar manner, the chemical sediments contain substances which have different antecedents, even though they were precipitated or crystallized from aqueous solutions in the locus of deposition.

Consequently, it is preferable, for geochemical purposes, to use another classification of the sediments. A classification based on geochemical principles was presented by Goldschmidt (1933*b*, 1934, 1945). A modification of this classification, adopted for the purposes of this book, is the following:

1. Resistates
2. Hydrolyzates
3. Oxidates
4. Reduzates
5. Precipitates
6. Evaporates
7. Bioliths

A schematic diagram of the main chemical characteristics of classes 1-6 of the sediments is presented in Figure 5.17, which is based on Goldschmidt's (1934) diagram.

The resistates, or residual sediments, consist of the chemically undecomposed weathering residues. This class includes chemically resistant coarse- and medium-grained materials. Upon deposition and diagenesis, quartz and ilmenite sands, gravels, sandstones, arkoses, conglomerates, etc., are formed.

The hydrolyzates consist partly of the chemically undecomposed, finely ground rock powder and partly of insoluble matter derived from hydrolytic decomposition during weathering. Bauxites, clays, shales, slates, etc., belong to this class.

The oxidates form by the precipitation of Fe^{3+} , Mn^{3+} , and Mn^{4+} ions as hydroxides. The deposition of the hydroxides is the result of

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oxidation of Fe^{2+} and Mn^{2+} salts in the oxygen-rich surface waters of lakes and seas. Iron and manganese ores of sedimentary origin are members of this group.

The reduzates are the opposites of the oxidates, inasmuch as they are formed in strongly reducing surroundings. Sulfides of sedimentary origin are often present in marine muds that are deposited in land-locked waters and in other places of poor circulation.

The precipitates form by inorganic precipitation from aqueous solutions, i.e., when the solubility product of the dissolved compound is exceeded. Precipitation may result when temperature decreases (e.g., deposition of silica from hot springs) or when chemical changes take place (e.g., decomposition of calcium bicarbonate and the subsequent precipitation of calcium carbonate). Marine, lacustrine, and

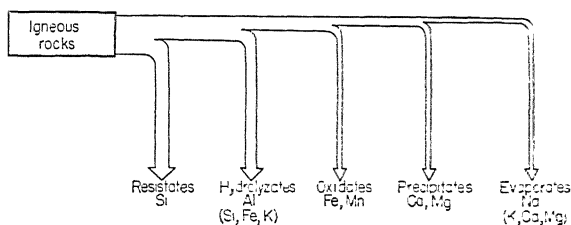


FIG. 5.17.—Chemical characteristics of sediments formed during weathering, transportation, and sedimentation.

other deposits of inorganically precipitated calcium carbonate and magnesium carbonate are examples of the precipitates.

The evaporates are those sediments which are deposited from aqueous solution as a result of extensive or total evaporation of the solvent.

The bioliths, or organogenic sediments, will be discussed in chapter 8 because many bioliths cannot be included in the first six groups of sediments listed above. However, the bioliths often occur together with the other sediments. Calcium carbonate of organic origin may occur along with inorganically precipitated calcium carbonate, and mud layers containing organic matter may be found in the company of clays.

It must be emphasized that the geochemical division of the sediments is not categorical. The sedimentation processes in Nature are continuous, and consequently the deposited sediments and their derivatives usually are mixtures of sediments belonging to two or three groups. Thus, e.g., clays may contain calcium carbonate and ferric hydroxide, or organic matter. Moreover, the boundary between

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the precipitates and the evaporates cannot always be sharply determined.

RESISTATES

The pure resistates represent the chemically unchanged residue from weathering. They are usually coarse grained and possess a more or less pronounced clastic texture. They are deposited in shallow water on the continental shelves, in lakes, and in the arid desert regions as boulders, gravel, and sand and are converted in diagenesis into conglomerates, graywackes, and various sandstones. A part of the fine-grained loess deposits also belongs to the resistates. Because chemical changes taking place during decomposition are never complete, the resistates contain the chief rock-making minerals of the original rocks. During weathering, however, those minerals which are

TABLE 5.44
AVERAGE MINERALOGICAL COMPOSITION
OF SANDSTONES

Constituent	Per Cent by Weight
Quartz (free silica).....	66.8
Feldspar	11.5
Argillaceous matter....	6.6
Limonite.....	1.8
Carbonates.....	11.1
Other minerals	2.2
Total .. .	100.0

stable against chemical decomposition and mechanical wear will become enriched in the sediments. Quartz is the most important among such minerals. It is the predominating or nearly sole constituent of certain resistates, particularly of sandstones. The dark rock-making minerals, e.g., biotite, amphibole, and pyroxene, are readily decomposed and consequently are impoverished in the resistates. Muscovite shares their fate.

The sandstones are, quantitatively, the most important resistates. Their average mineralogical composition, according to Clarke (1924), is presented in Table 5.44.

The comparison of the mineralogical composition of the sandstones with the mineralogical composition of igneous rocks (see Table 5.16) at once reveals the strong enrichment of quartz in the sandstones. The feldspars are quantitatively far the most important rock-making constituents of igneous rocks, but in sandstones they occupy a subordinate position. In arkoses, however, the feldspars occur as one of the predominating constituents. The amphiboles and pyroxenes,

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which, on the average, are quantitatively more important constituents in igneous rocks than quartz is, are nearly totally absent in sandstones. In a similar manner the micas do not occur among the typical constituents of the sandstones. Argillaceous material, limonite, and carbonate minerals, even though present in sandstones as cementing substances, are geochemically irrelevant to these rocks.

Freise (1931, 1932) carried out experimental research on the abrasion of minerals and rocks by flowing water. His results showed that

TABLE 5.45
TRANSPORTATION RESISTANCE OF MINERALS COMPARED
WITH TRANSPORTATION RESISTANCE OF
COMPACT HEMATITE (100)

Mineral	Relative Transportation Resistance
Galena.....	75
Monazite.....	105-130
Orthoclase.....	150
Diopside.....	160
Quartz.....	245
Olivine.....	250
Zircon.....	265
Apatite.....	275
Ilmenite.....	325
Sphalerite.....	350
Cassiterite.....	360
Almandite.....	375
Magnetite.....	380
Topaz.....	390
Staurolite.....	420
Augite.....	420
Wolframite.....	450
Rutile.....	455
Chromite.....	475
Pyrite.....	500
Corundum (sapphire).....	750
Tourmaline.....	650-950

in the disaggregating rocks the micas are consumed first, followed by feldspars and feldspathoids, amphiboles and pyroxenes, quartz, titanium minerals, and other accessory constituents. Freise (1931) also gave relative transportation resistance values for a number of minerals. The more important values are presented in Table 5.45.

With the exception of monazite the accessory constituents, which have higher specific gravity than quartz and feldspar, have higher relative transportation-resistance values than do the two minerals. Therefore, by the action of wind, flowing water, and especially waves, they often become concentrated in bands and layers of varying thickness which may be used as technically valuable ores, such as the

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monazite placers of Brazil and the cassiterite deposits of Malaya. Such stream, beach, and glacial deposits of heavy minerals often occur in consolidated sandstones as well-preserved layers which may show local variations in their petrographic character.

Freise (1932) found that basic rocks are much more readily worn by flowing water than are acidic rocks. Metamorphic rocks (schists), according to his experiments, were considerably more stable against stream abrasion than were igneous rocks of a similar mineralogical composition. The decomposing action of flowing water is nearly exclusively mechanical, and the chemical processes caused by dissolved substances are commonly less important.

HYDROLYZATES

The argillaceous substances formed during weathering and other comparable substances are the foremost representatives of the hydrolyzate sediments. The hydrolyzates are characterized by their occurrence as solid insoluble particles already in the site of weathering and by their transportation as suspended particles to the loci of sedimentation by the action of flowing water and of other geological agents. They differ from the resistates by their decidedly smaller particle size: often the hydrolyzate grains have the dimensions of colloidal particles.

The petrographic study of the important hydrolyzates, viz., clays, bauxites, and laterites, has been greatly handicapped by their small particle size. It was previously held that the clays are chiefly composed of amorphous gels, which remain as insoluble products of hydrolysis during the weathering. However, ever since the application of modern X-ray diffraction analysis and electron microscopic methods to the study of clays, silts, and other hydrolyzate sediments, it is known that nearly all clays are composed almost entirely of crystalline materials and that the amorphous gels play a subordinate role in their mineralogical composition. The crystalline clay minerals are the dominant constituents of clays. Among the clay minerals, only allophane is amorphous. It is well to remember that gels and colloidal particles are not necessarily amorphous substances. A colloidal particle may have an organized crystal structure, and therefore it must be considered a mineral.

The clays consist of residual mineral particles or of the chemically unchanged weathering residues, of the clay minerals proper that

are formed during weathering, of biogenic matter, and of minerals formed in the sediment after its deposition.

Quartz is the foremost weathering residue of the argillaceous sediments. It is commonly rather abundant. Feldspar is present in notable amounts, and micas and sometimes primary calcite may be found as weathering residues.

The siliceous and calcareous tests of organisms and organic matter represent biogenic material in the hydrolyzates.

The minerals formed after the deposition of the hydrolyzates include, among others, pyrite, glauconite, dolomite, and ferromagnesian (breunnerite, mesitite), $(\text{Mg,Fe})\text{CO}_3$. These minerals are of secondary origin, and their formation is a part of the diagenetic processes.

The clay minerals are, geochemically, the most important constituents of argillaceous sediments. As products formed in hydrolysis, they either are totally irrelevant to igneous rocks or form therein only under special circumstances, e.g., under hydrothermal conditions. So far, the classification of the clay minerals cannot be considered final, the reason being that their identification by means of the commonly used petrographic methods is impossible because of their small particle size. Therefore, their identification is carried out chiefly with X-ray diffraction studies and electron microscopy. The former method also allows the semiquantitative determination of the mineralogical composition of mixtures of clay minerals. However, the studies are handicapped by the fact that many structurally different clay minerals have similar bulk composition and that some clay minerals with different bulk composition have nearly analogous crystal structure and therefore cannot be distinguished from one another by means of their X-ray diffraction patterns. The following clay minerals have been identified in argillaceous sediments:

- a) Kaolinite group
Kaolinite, dickite, nacrite, $\text{Al}_4[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$
Anauxite, $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- b) Montmorillonite group
Montmorillonite, $\text{Al}_2[(\text{OH})_2|\text{Si}_4\text{O}_{10}] \cdot n\text{H}_2\text{O}$
Beidellite, $\text{Al}_2[(\text{OH})_2|\text{AlSi}_3\text{O}_8\text{OH}] \cdot n\text{H}_2\text{O} (?)$
Nontronite, $\text{Fe}_2^{2+}[(\text{OH})_2|\text{Si}_4\text{O}_{10}] \cdot n\text{H}_2\text{O}$
- c) Halloysite-metahalloysite group
Halloysite, $\text{Al}_4[(\text{OH})_8|\text{Si}_4\text{O}_{10}] \cdot 4\text{H}_2\text{O}$
Metahalloysite, $\text{Al}_4[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$
- d) Illite group
Illite (bravaisite), approximately $2\text{K}_2\text{O} \cdot 3(\text{Mg,Fe})\text{O} \cdot 8(\text{Al,Fe})_2\text{O}_3 \cdot 24\text{SiO}_2 \cdot 12\text{H}_2\text{O}$
Glauconite, $\text{K}_{2-3}(\text{Mg,Fe}^{2+},\text{Ca})_{1-3}(\text{Fe}^{3+},\text{Al})_{3-6}[(\text{OH})_8|\text{Al}_{3-2}\text{Si}_{12-14}\text{O}_{40}]$

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- e) Magnesium-rich clay minerals
Sepiolite, $\text{Mg}_3[(\text{H}_2\text{O})_3|\text{Si}_4\text{O}_{11}]\cdot\text{H}_2\text{O}(?)$
Attapulgite, $\text{Mg}_{2.5}\text{H}[(\text{H}_2\text{O})_3|\text{Si}_4\text{O}_{11}]\cdot\text{H}_2\text{O}$
- f) Allophanes
Allophanite, $x\text{Al}_2\text{O}_3\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$
- g) Chloritic mica
- h) Oxides and hydroxides
Hydrargillite (gibbsite), $\gamma\text{-Al}(\text{OH})_3$
Diaspore, $\alpha\text{-AlOOH}$
Boehmite, $\gamma\text{-AlOOH}$

This list shows that hydrous aluminum silicates predominate among clay minerals. Moreover, it must be noticed that the clay minerals may contain calcium and magnesium (montmorillonite, beidellite; because the position occupied by Mg^{2+} and Ca^{2+} in the structure is still unknown, these metals were not considered in the formulas given above), ferric iron (nontronite), and magnesium (sepiolite, attapulgite). In the montmorillonite group, Al^{3+} is known to be replaced by Mg^{2+} , Fe^{3+} , and Cr^{3+} , and small quantities of Li^+ , Mn^{2+} , and Ni^{2+} may also be present.

The groups of major importance among the clay minerals are the illite group, the montmorillonite group, and the kaolinite group. The other groups are of minor importance as constituents of clays. The magnesium-rich clay minerals are, so far, relatively little known. Dickite, nacrite, and anauxite of the kaolinite group are rare constituents of clays.

Illite is the most abundant clay mineral of recent marine sediments, whereas kaolinite is somewhat less widely distributed and montmorillonite is only a minor constituent. In sedimentary clays either kaolinite or illite may dominate. Montmorillonite and halloysite occur as accessory constituents. Illite usually predominates in shales of marine origin, in the argillaceous material of till and loess, and in many soils. The montmorillonite group is abundant in many bentonite clays, which are formed by the alteration of glassy volcanic ash.

Kaolinite probably is the most stable of the clay minerals. The formation of kaolinite or of montmorillonite and beidellite during weathering seems to depend on the order of breakdown of minerals in the parent-rock (Ross, 1943). If the ferromagnesian minerals and the feldspars are decomposed simultaneously, ferrous and ferric iron, magnesium, alumina, and silica will be released, and the formation of montmorillonite or beidellite follows. If the ferromagnesian minerals break down first, magnesium is removed in solution and iron

either removed or precipitated as hydroxide or oxide under extremely oxidizing conditions. When the feldspars decompose, no magnesium and iron are available, and kaolinite will form. Moreover, kaolinite forms when leaching is effective and weathering is thorough, whereas montmorillonite results in soils in which drainage is poor and oxidation restricted. Kaolinite forms both under oxidizing and reducing conditions, in the presence of organic matter, such as humic complexes, and in the presence of organic acids. According to Ross (1943), it is evident that the removal of magnesium, calcium, the alkali metals, and ferrous iron by the action of acid solutions and of organic compounds is the essential factor in the formation of kaolinite. The presence of ferrous iron in the weathering solutions favors the formation of montmorillonite, but, if iron is removed or oxidized, the effect is destroyed.

Clay minerals also occur in hydrothermal veins and mineral deposits. Members of the kaolinite, illite, and montmorillonite group have been found in such formations. The formation of clay minerals under hydrothermal conditions depends on the pH of the solutions; it is discussed in chapter 17.

The chemical composition of the various clay minerals is presented in Table 5.46, which is based on the collection of analyses published by von Engelhardt (1937) and by Grim, Bray, and Bradley (1937). The analyses give the composition of pure samples of the clay minerals.

The crystal structure of some clay minerals (silicates) is schematically presented in Figure 5.18. The structure of muscovite is presented for comparison. Anauxite differs from kaolinite chemically by its higher silica content, but its structural details are still unknown. This is the case also with beidellite, which, however, may structurally resemble montmorillonite. According to Grim (1942), beidellite is a mixture of montmorillonite and limonite. All members of the montmorillonite group have an expanding structure. Metahalloysite is formed by the dehydration of halloysite. Structurally, it rather closely resembles kaolinite. The structures of clay minerals rich in magnesium are still incompletely known. They probably have a fibrous, instead of a sheet, structure. The structure of illite is similar to that of montmorillonite, but in illite about 15 per cent of the Si^{4+} ions are replaced by Al^{3+} , and K^{+} ions enter between the sheets of two neighboring units to compensate for the excess negative charge. Therefore, the structure of illite is similar to that of muscovite. The illites differ

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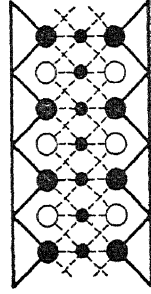
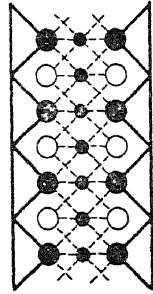
chemically from muscovite only by their lower alkali content and higher water content.

The clay minerals rich in magnesium are structurally inadequately known. All the other silicate constituents of clays have typical sheet structures. With the exception of illite, they differ from mica in so far as their structural sheets are not connected by means of cations, such as the potassium ions in muscovite. Therefore, it follows that the bond between the sheets in clay minerals is weaker than in the

TABLE 5.46
CHEMICAL COMPOSITION OF SOME CLAY MINERALS FROM THE UNITED STATES
(Composition Given in Per Cent by Weight)

Constituent	Kao-linite, Staten Island, N.Y.	Anauxite, Moke-lumne River, Lancha Plana, Calif.	Montmorillonite, Pala, San Diego Co., Calif.	Beidel-lite, Beidell, Saguache Co., Colo.	Non-tronite, Woody 1, Calif.	Halloy-site, Hickory, N.C.	Metahal-loysite, Brandon, Rankin Co., Miss.	Illite, Gilead, Calhoun Co., Ill.	Attapul-gite, Attapul-gus, Ga.
SiO ₂	46 44	52.46	50 06	47 28	47 51	44 08	44 68	50 10	51.28
Al ₂ O ₃ ...	36 36	32 20	21 32	20.27	0.37	39 20	38 59	25.12	10.56
Fe ₂ O ₃ ...	1.25	1.69	0 22	8 68	35 17	0 10	0 39	5 12	6 76
FeO.....	n.d.	n.d.	trace	n.d.	0.00	n.d.	n.d.	1.52	n.d.
MnO....	0 03	n.d.	0 13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO....	0.18	0 00	4 42	0 70	1 40	n.d.	0 08	3.93	10.40
CaO....	0.28	0 03	1.26	2.75	2 50	n.d.	0 18	0.35	1.44
Na ₂ O....	0.42	0 25	0 33	0.97	0 09	0 20	0 11	0 05	n.d.
K ₂ O....	1.50	0 31	0.19	trace	0 06	n.d.	0 05	6.93	n.d.
H ₂ O+....	11.46	12 07	}21.62	}19 72	5 90	}16 18	14 90	} 6.82	}20.28
H ₂ O-....	0.69	1.38			7 16		1 55		
TiO ₂	0.84	0 55	trace	n.d.	0 00	n.d.	n.d.	0.50	n.d.
Total	99.45	100 94	99.55	100 37	100 16	99 76	100 53	100.44	100 72

micas. This conclusion explains their eminent cleavage parallel to the basal plane, which seems to be still more easy than in the micas. The perfect cleavage may also partly explain the observation that the clay minerals never are found as large crystals. Because the bond between the sheets is relatively weak, the structure cannot attain large dimensions in the direction of the *c*-axis but breaks down rather readily. The weakness of bond between the sheets is further displayed, in the montmorillonite structure, by the observation that the distance between two adjacent layers is not a structural constant but may increase or decrease according to the tension of water vapor. Consequently, water molecules are added to, or removed from, the space between the layers in the structure. Therefore, the structure as



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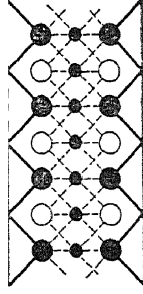
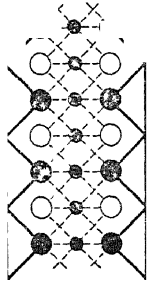
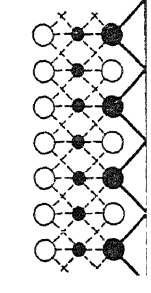
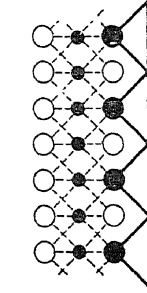
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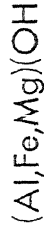
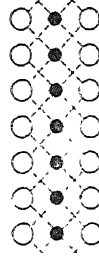
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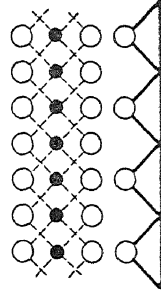
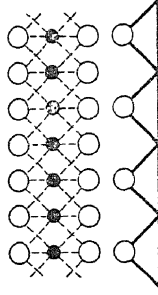
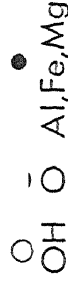


morillonite



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Halloysite



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a whole may expand or contract in the direction of the *c*-axis, and this phenomenon evidently is one of the causes of the hygroscopic properties of montmorillonite. The eminent cleavage of the clay minerals materially promotes their abrasion during transportation and consequently is a partial cause of their extremely small particle size in sediments.

Among the rock-making minerals of igneous rocks the feldspars are quantitatively the most important, and the same conclusion follows for the uppermost parts of the lithosphere in general. The feldspars, moreover, contain the bulk of aluminum present in igneous rocks. Consequently, the manner of decomposition of the feldspars must be known, in order that the processes leading to the formation of clay minerals may be understood. Correns and von Engelhardt (1939; von Engelhardt, 1939) showed that the feldspar is completely dissolved as ions, during weathering by the action of solutions with pH 3–11 which are found in Nature. The alkali metals and calcium are first extracted, and an extremely thin layer, enriched in silica and alumina, remains on the surface of the feldspar grains, but this layer also gradually goes into solution. Along with the ions, the weathering solutions may contain very small ion-like complexes, but definitely no colloidal particles. At elevated temperatures (tropical weathering) the feldspar dissolves in a neutral solution (pH 6–7) more rapidly than at lower temperatures, but no other differences exist in the solution process. Later research on leucite and tremolite has shown that their decomposition is similar to that of the feldspars. The ionic solutions may give rise to new minerals: aluminum and silica react with each other, and clay minerals are formed. Contrary to previous belief that the clay minerals are undissolved weathering residues, the results of Correns and von Engelhardt show that the clay minerals actually are generated as the result of the reaction between Si^{4+} and Al^{3+} ions in the extremely dilute weathering solutions. However, the mica-like clay minerals may, perhaps, form by the incomplete extraction of alkali metals from micas, and then the original micaceous structure has remained as a relic.

The weathering processes resulting in the formation of clays are characterized by the leaching-out of the alkali metals, particularly of sodium, of calcium, and of a part of magnesium. The impoverishment in these metals also characterizes the argillaceous sediments in general. Some analyses of clays and of their derivatives are presented in Table 5.51.

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Unlike the argillaceous sediments, the laterites and bauxites are decidedly impoverished in silica. Along with the alkali metals, calcium, and magnesium, silica is nearly completely leached out, and chiefly ferric hydroxide and aluminum hydroxide remain in the sediments that show varying Fe:Al ratios. The laterites are typical products of tropical and subtropical weathering. Often they cover extensive areas and occur *in situ* on the weathered rock. However, there are also transported laterites which always contain finely ground quartz particles and clay minerals. Like the argillaceous sediments,

TABLE 5.47
CHANGES IN CHEMICAL COMPOSITION DURING WEATHERING IN
TEMPERATE AND TROPICAL ZONES
(Composition Given in Per Cent by Weight)

CONSTITUENT	DOLERITE ROWLEY REGIS, SOUTH STAFFORDSHIRE, ENGLAND		DOLERITE WESTERN GHATS, BOMBAY, INDIA	
	Fresh Rock	Overlying Clay	Fresh Rock from Poonah	Overlying Laterite from Mahabaleshwar
SiO ₂ ...	49.3	47.0	50.4	0.7
Al ₂ O ₃ ...	17.4	18.5	22.2	50.5
Fe ₂ O ₃ ...	2.7	14.6	9.9	23.4
FeO ...	8.3		3.6	
MgO ...	4.7	5.2	1.5	
CaO ...	8.7	1.5	8.4	
Na ₂ O ...	4.0	0.3	0.9	
K ₂ O ...	1.8	2.5	1.8	
H ₂ O ...	2.9	7.2	0.9	25.0
TiO ₂ ...	0.4	1.8	0.9	0.4
P ₂ O ₅ ...	0.2	0.7		
Total ..	100.4	99.3	100.5	100.0

which are characterized by clay minerals, the laterites and bauxites contain characteristic minerals, mainly hydrous oxides of ferric iron and aluminum. So far these minerals are still less known than the clay minerals. They include hydrargillite, diaspor, and boehmite.

The differences between the weathering processes leading to the formation of clays and laterites are illustrated by the analyses of two chemically closely similar rocks and their weathering products, given in Table 5.47, according to Warth (1905).

The process of primary lateritization is followed by the addition of silica, whereby many laterites change into quartziferous and impure kaolins. Only in areas with high rainfall and good drainage are the laterites permanent.

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The role of amorphous gels as constituents of laterites is negligible, just as it is in argillaceous sediments. Their content is small compared with the content of the hydrous oxides. Many of the hydrous oxide minerals resemble structurally the silicate minerals of the hydrolyzates, inasmuch as they have more or less flaky structures.

SOILS

Soils are composed of inorganic and organic materials. They occur on the surface of the Earth and support the continental plant life. The character of the soil depends on the nature of the weathering of their substratum, which is the surface of the lithosphere. Consequently, physical, chemical, and biological processes are active in the formation of soil.

Moreover, the general nature of the soil depends on climate, relief, organisms, and time, whereas the parent-material seems to be of less importance. In a temperate humid climate the uncultivated soil usually consists of a thin layer of plant remains, which is underlain by a layer of mineral and organic matter called the topsoil. Below is a layer developed by the action of micro-organisms in the overlying horizons. The humic complexes and the organic compounds produced by the micro-organisms and dissolved in rain water have leached out compounds of iron and aluminum. Clay minerals are also transported downward by the plentiful percolating solutions, and a layer relatively rich in silica is thus produced. The iron and aluminum compounds, the dissolved silica, and the organic colloids are redeposited in the lower zone, which is called the horizon of accumulation; but the readily soluble sodium, calcium, and magnesium salts and colloidal silica are removed by ground water. Much potassium and some magnesium are retained by the clay minerals in the horizon of accumulation. The kaolinite group normally predominates among the clay minerals of soil.

The migration of some elements in forest soil is discussed in chapter 8. The soils formed by the processes described above are called podzolic soils and the process itself is called podzolization, which is the normal soil-making process in a temperate humid climate in the presence of forest vegetation.

Another type of soil occurs in dry plains. In this type the topsoil is rich in organic matter, and the zone of accumulation below does not materially differ from the topsoil, because the amount of rainfall is low and the rate of evaporation is high, and consequently the

amount of leaching caused by percolating solutions is negligible. Only the most soluble compounds of the alkali metals are removed, whereas the alkaline-earth metals remain as carbonates. In this type of soil the partial decomposition is followed by deposition of calcium carbonate and of some magnesium carbonate in the zone of accumulation, often in the form of concretions. The process is called calcification. It occurs mainly in the presence of a grass or brush vegetation in a relatively dry climate and at temperatures high enough to assure the destruction of the plant remains at a comparatively rapid rate. The rate of chemical weathering within the soil is rather low. Soils of this type include the caliche and chernozem soils. The latter are believed to be the most fertile natural soils. They occur in the plains of Russia and of America.

Still another group of soils is formed as the product of weathering in a subtropical and tropical climate. The rate of chemical weathering is high, the plentiful rains remove most of the products formed, and consequently very little material actually is deposited in the horizon of accumulation. The thickness of the weathered zone may be as high as 25 meters. Notwithstanding the thriving vegetation, micro-organisms decompose the plant remains at a rapid rate, most of the humic compounds are oxidized to carbon dioxide, and therefore very little organic matter accumulates, facilitating the solution of iron and aluminum compounds. Silica goes readily into solution, whereas the iron and aluminum compounds accumulate on the surface of the soil. Red lateritic soils are formed by these processes, which are called lateritization. The manner of lateritic weathering varies from place to place, and its details are still incompletely understood.

Clays, consisting chiefly of kaolinite, are in many places the stable end-products of weathering under tropical conditions, but often the clay minerals decompose, and hydroxides or oxides of ferric iron or aluminum, or both, accumulate. The degree of enrichment of iron in the laterite soils may be high enough to result in the formation of workable ores.

Lateritization is not totally confined to tropical climates. Poor drainage in temperate zones may cause local accumulation of aluminum hydroxide in soil. The terra rossa soils, which consist of ferric oxide, aluminum hydroxide, and relatively large amounts of alkaline-earth compounds and which occur in the Mediterranean countries, may be comparable to the laterites, because the accumulation of humic matter is prevented by the hot, dry summers (Reiche, 1945).

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Along with climate and vegetation, the chemical composition of the parent-material to some extent determines the properties of the soil. This material may be residual, lying *in situ* on the disintegrating rocks, or it may be transported by the action of various geological agents.

The inorganic constituents of soil, or the soil minerals, consist of the unweathered remains of the disintegration of the parent-rocks or of the original transported material, along with a number of decomposition products. Quartz, clay minerals, limonite, and hematite are the most important mineralogical constituents of soil. Carbonate and sulfate minerals may also be present except in areas of considerable rainfall.

Clay minerals make up an essential part of soil. Their base-exchange capacity (see below) affects the fertility of the soil. The high replaceability of Ca^{2+} provides a readily available source of calcium in soils containing minerals of the montmorillonite group. Kaolinite, illite, and probably halloysite occur in soil, along with montmorillonite. Some soils contain several clay minerals, whereas others show a tendency to be monomineralic.

Organic matter greatly affects the physical properties and the fertility of soil. Moreover, it is the cause of the reducing capacity of soil, the prime result of which is the reduction of ferric to ferrous iron and the solution and removal of a number of elements, such as iron, manganese, and aluminum, as humic complexes. Consequently, organic matter affects the weathering and transportation of the inorganic constituents of soil.

Among the organic constituents of soil the humic complexes are the most important. Humus, however, belongs to the biosphere and consequently will be discussed in chapter 8. Living organisms also play an important role in soil processes and may modify the chemical composition of the soil in an indirect way; for example, micro-organisms affect the cycle of oxygen, nitrogen, and sulfur in soil.

It should be noted that many sediments obtain a part of their material from the soil.

OXIDATES

The oxidates are sediments formed by oxidation. Unlike the resistates and hydrolyzates, which are transported as particles of varying size that are suspended in solution or by other means, the oxidates are formed from material carried in ionic or colloidal solution to the site of deposition, where oxidation takes place. The material

of the oxidates is carried partly in ground water, partly by surface waters. The hydroxides of ferric iron and of manganese form the bulk of the oxidates. These hydroxides are precipitated in lakes and shallow bays and sometimes even on the bottom of the open ocean.

Natural waters contain iron either as ferrous bicarbonate, $\text{Fe}(\text{HCO}_3)_2$, and ferric fluoride, FeF_3 , which are rather incompletely dissociated compounds, or as colloidal ferric hydroxide and ferric phosphate. Ferrous bicarbonate is readily soluble, but in the presence of molecular oxygen it is promptly oxidized, and ferric hydroxide precipitates. Colloidal ferric hydroxide, on the other hand, is rather stable in solution, and its stability is further increased by the presence of suitable protective colloids. In oxygen-bearing waters the substances acting as protective colloids are gradually oxidized, and ferric hydroxide precipitates. The precipitation of iron as ferric hydroxide may also start when the protective action of the colloids decreases or ceases altogether, as the solutions enter surroundings rich in dissolved electrolytes. The precipitation of iron may be inorganic, but it may also take place under the direct or indirect action of microorganisms. The precipitation of manganese as hydroxide is largely similar to the precipitation of iron.

Iron and manganese ores of sedimentary origin are the most important representatives of the oxidates. Goethite, $\alpha\text{-Fe}^3\text{-OOH}$, is the chief mineral of the iron-rich oxidates, whereas lepidocrocite, $\gamma\text{-Fe}^3\text{-OOH}$, hematite, magnetite, and silicate minerals of iron are rarer constituents (see chap. 33). The silicates have a mica- or chlorite-like structure, which so far is unknown in details. Cronstedtite, $\text{Fe}_4^2+\text{Fe}_2^3+[(\text{OH})_8[\text{Fe}_2^3+\text{Si}_2\text{O}_{10}]]$, which resembles kaolinite structurally, is also present in the iron ores of sedimentary origin. The oxide ores of manganese contain trivalent and quadrivalent manganese as hydroxide or oxide, but their constituent minerals still are largely unknown.

The cycle of manganese and iron, respectively, and the formation of their oxidate deposits are treated in chapters 31 and 33.

Two analyses of oxidate sediments, according to Clarke (1924), are presented in Table 5.48.

REDUZATES

Coal and petroleum, which are organogenic sediments and will be treated in chapter 8, are the most important reduzates. The reduzates also include a number of muds which are deposited in water and con-

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sist essentially of hydrolyzate and oxidate material and of organisms and their remains in a state of decomposition and decay. The formation of mud requires the presence of reducing environments in which the organic matter cannot completely oxidize. Reducing surroundings may become established where the currents carrying oxygen-bearing surface water do not reach the bottom or where the surface waters have been deprived of their oxygen by biological activity. The reduzate muds are characterized by their considerable sulfur content.

TABLE 5.48
ANALYSES OF OXIDATES
(Composition Given in Per Cent by Weight)

Constituent	Limonite (Bog Iron), Mittagong, Australia	Wad (Bog Manganese), Romanèche, France
Fe ₂ O ₃	65.84	} 1.10
Al ₂ O ₃	4.49	
MnO ₂	n.d.	64.98
MnO	1.40	7.27
MgO	0.48	trace
CaO	trace	1.65
BaO	n.d.	15.45
PbO	n.d.	0.30
CuO, ZnO, CoO	n.d.	trace
Na ₂ O	n.d.	0.80
K ₂ O	n.d.	trace
H ₂ O+	10.86	} 5.00
H ₂ O-	2.30	
SiO ₂	14.27	0.80
P ₂ O ₅	0.25	0.05
As ₂ O ₅	n.d.	0.60
SO ₃	0.11	n.d.
CaSO ₄	n.d.	0.40
Insoluble	n.d.	1.40
Total	100.00	99.80

The scarcity or total absence of oxygen has prevented the oxidation of sulfur to sulfate, and therefore free hydrogen sulfide is present in the deep waters. Hydrogen sulfide precipitates a number of siderophile and chalcophile metals as sulfides. Iron is precipitated either as monosulfide or as disulfide. The iron sulfides are present in the sediment as finely divided pyrite and marcasite or as melnikovite, a cryptocrystalline pyrite. The sulfur of the reduzates is partly derived from the sulfoproteins present in the organic matter when the remains of the organisms decay and partly produced by the reduction of soluble sulfates of sea water and of insoluble sulfates of the sedi-

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ments by the action of sulfur bacteria. Analyses of some reduzates are presented in Tables 8.7 and 8.9.

PRECIPITATES

The precipitates are formed in aqueous solutions when the solubility product of one or several of the dissolved constituents is exceeded for other reasons than the evaporation of the solvent. The material of the precipitates, like the material of the oxidates, is originally dissolved in water, but in the case of the precipitates the solution always is an ionic solution and never a colloidal one. The most important precipitates are essentially carbonates of calcium, magnesium, and iron. Impurities consisting of resistates (sand) and hydrolyzates (clay) are commonly met in the precipitate beds.

The precipitates are partly marine, partly continental in origin. Their predominant constituent is calcium carbonate, which occurs in Nature in four different forms, viz., as calcite, aragonite, vaterite ($\mu\text{-CaCO}_3$), and amorphous carbonate. Under atmospheric pressure calcite is the stable form, and the other modifications are gradually converted into calcite. The bulk of the carbonate sediments consists of calcite, but these sediments may also contain small amounts of aragonite, formed either by inorganic precipitation or by the action of organisms. So far, it is unknown whether calcium carbonate originally may become deposited as vaterite, which later would be converted into aragonite or calcite. Vaterite, however, is reported to occur in the skeletons of some gastropods.

The continental calcareous precipitates include calcium carbonate precipitated in lakes and the calcareous tufas and sinters and the travertines deposited by hot springs. It is evident that the sediments deposited by hot springs must be considered precipitates unless they are formed by the extensive evaporation of volcanic solutions. Thus many borate deposits belong to this group, even though their boron in some cases may derive from weathering solutions.

Calcium carbonate deposited in lakes and around springs is formed as a result of the escape of carbon dioxide from the water, whereby the solubility of calcium carbonate decreases. The loss of carbon dioxide may be the result of the release of pressure when the water reaches the surface, of an increase in temperature, of agitation, or of the biological activity of green plants. The marine carbonate sediments are deposited either by a purely chemical precipitation from saturated or supersaturated sea water or by the accumulation of cal-

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careous shells and skeletons of lime-secreting marine organisms. Quantitatively, the marine calcium carbonate sediments far exceed the terrestrial ones. The formation of the calcareous sediments is discussed in chapter 15.

A notable part of the precipitates consists of dolomite, $\text{CaMg}[\text{CO}_3]_2$. Structurally, dolomite differs only slightly from calcite: the positions of the Ca^{2+} ions in the calcite structure in dolomite are alternately occupied by Ca^{2+} and Mg^{2+} ions. The Mg^{2+} ion may be partly replaced by Fe^{2+} , from which ankerite, $\text{Ca}(\text{Mg,Fe})[\text{CO}_3]_2$, results. Ankerite forms isomorphic mixtures with dolomite. All gradations probably exist between pure calcitic limestones and pure dolomites. As much as 25 per cent MgCO_3 may be present in the tests and skeletons of lime-secreting organisms, but a notable part of the dolomitic limestones has been formed from calcitic limestones through the metasomatic addition of magnesium. The dolomitization begins in the sea, where it is caused by the magnesium salts dissolved in sea water. The process continues during diagenesis and takes place still later, when the carbonate sediments are no longer directly connected with sea water. The possibility cannot be excluded that dolomite may form by direct precipitation in the sea. The relatively common occurrence of dolomite in Nature is in full agreement with the thermochemical observation that dolomite is stable in the conditions met in Nature, whereas the corresponding mixture of calcite and magnesite is unstable. Magnesite, MgCO_3 , does not commonly form independent sediments, but siderite, FeCO_3 , is deposited in the absence of oxygen. However, geochemically the siderite sediments are relatively unimportant. Other minerals formed by precipitation under reducing conditions include ferromagnesite, $(\text{Mg,Fe})\text{CO}_3$, pyrite and marcasite, FeS_2 , hydrotroilite, $\text{FeS} \cdot n\text{H}_2\text{O}$, and melnikovite, the cryptocrystalline pyrite. They are present in certain types of marine sediments.

Siliceous sinter or geyserite is precipitated from the waters of hot springs. It is commonly suggested that most chert and flint bodies are precipitated inorganically near the inlets of rivers into the sea. However, in sea water the flocculation of the extremely diluted silica sols is impossible, and consequently the inorganic origin of siliceous deposits in the sea under normal conditions seems to be excluded. The siliceous sediments formed by the deposition of the silica shells of diatoms are comparable in origin with the organically precipitated

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carbonate sediments. The accumulation of the diatom tests may produce technically valuable diatom oozes and diatomite deposits.

Most of the phosphate sediments are precipitated through organic agencies, but some calcium phosphate is formed by inorganic precipitation, probably when calcium carbonate or calcium fluoride is present. Collophane, the microcrystalline carbonate-fluorapatite, and

TABLE 5.49
ANALYSES OF SOME PRECIPITATES
(Composition Given in Per Cent by Weight)

Constituent	Travertine, Terrace Moun- tain, Mammoth Hot Springs, Yellowstone Nat'l Park, Wyoming, U.S.A.	Geyserite Incrustation, Giant Group, Upper Basin, Yellowstone Nat'l Park, Wyoming, U.S.A.	Iron Carbonate, Sunday Lake, Michigan, U.S.A.	Oceanic Phos- phatic Concretion from a Depth of 1,900 Fathoms, Challenger Expedition
SiO ₂	0 09	72.25	28.86	2 56
Al ₂ O ₃	} 0.11	10 96	1.29	1 43
Fe ₂ O ₃		0.76	1.01	2 79
FeO	n.d.	0.31	37.37	n.d.
MnO	n.d.	n.d.	0.97	n.d.
MgO	0 35	0.10	3.64	0 83
CaO	55.37	0 74	0.74	40 95
Na ₂ O	n.d.	3 55	n.d.	n.d.
K ₂ O	0.04	1.66	n.d.	n.d.
NaCl	0.10	0.36	n.d.	n.d.
SO ₃	0.44	0.45	n.d.	1.39
CO ₂	43.11	n.d.	25.21	10 64
C	n.d.	0.20	n.d.	n.d.
TiO ₂	n.d.	n.d.	0.20	n.d.
P ₂ O ₅	n.d.	n.d.	n.d.	23.54
H ₂ O	0.32	9 02	0.68	3 65
C, organic	0.17	n.d.	n.d.	n.d.
Insoluble residue	n.d.	n.d.	n.d.	11 93
Total	100.10	100 36	99 97	99 71

dahllite (oxyfrancolite) are the chief phosphate minerals present in marine phosphate nodules (see chap. 24).

Native sulfur is sometimes precipitated inorganically in marine sediments. The sulfates barite, Ba[SO₄], and celestite, Sr[SO₄], and the carbonates witherite, BaCO₃, and strontianite, SrCO₃, are of minor geochemical importance as precipitates. Authigenic feldspars, tourmaline, and other minerals found in sediments may also be considered precipitates, but their geochemical significance is small.

Analyses of some precipitates are presented in Table 5.49 and are taken from Clarke (1924).

EVAPORATES

The material of the evaporates, like the material of the precipitates and a part of that of the oxidates, is present in natural waters in ionic solution. The evaporates, however, differ from the precipitates and oxidates in so far as, being readily soluble, they cannot be directly deposited under normal conditions but require the extensive and exceptional evaporation of the solvent for their deposition. The evaporation sometimes leads to the complete drying-up of seas, lagoons, gulfs, and lakes. According to their manner of occurrence, the evaporates may become deposited in such seas or shallow gulfs that, like the Karaboghaz Gulf in the eastern part of the Caspian Sea, are connected with the open sea only through a shallow and narrow channel. Moreover, such nearly isolated basins occur in arid regions in which the amount of precipitation is very small. The third condition is the absence of any appreciable drainage into the basin. Evaporates are also formed in closed basins in isolated inland areas, but, geochemically speaking, the quantities of evaporates formed therein are small as compared with the amount of evaporates formed in the seas and in adjoining basins.

The average salinity of ocean water is approximately 3.5 per cent and is generally lower in the polar seas than in the tropical seas; thus, e.g., the salinity of water in the Red Sea is 4 per cent. The Dead Sea with a salinity of 25.9 per cent, the Great Salt Lake with 27.7 per cent, and the Karaboghaz Gulf with 28.5 per cent are among the extremes in salinity. These and similar high contents of dissolved salts approach the saturation limit.

According to their manner of formation and occurrence the evaporates may be divided into the following groups:

1. Marine evaporates (salts crystallized from sea water)
2. Continental evaporates
 - a) Salts crystallized from ground water in arid and semiarid regions
 - b) Salts crystallized from inland lakes
 - c) Salts crystallized from hot-spring waters
 - d) Salts crystallized through the direct action of the constituents of air or of organisms

Marine carbonates and the deposits of hot springs, such as siliceous sinter, calcareous tufa, and ferric hydroxide, which are precipitated when their solubility product is exceeded, do not belong to the group of evaporates. However, the boundary between the precipitates and the evaporates is not always readily established. It has been customary to include in the group of evaporates only the relatively

readily soluble crystallates with a solubility at least comparable with that of calcium sulfate. At any rate, it is evident that both precipitates and evaporates may occur in the same deposit. Thus calcium carbonate or sulfate may first be precipitated inorganically prior to the evaporation of water, upon which a second generation of the same material may follow, which is deposited as a true evaporate.

The extensive salt beds of the Stassfurt area in Germany, which were deposited from the Permian Zechstein Sea, form the best illustration of marine evaporates. They are geochemically of high importance because they contain the complete series of the crystallized salts formed by the total evaporation of sea water. Marine evaporates are common in the geological column, but they seldom form a complete and undisturbed series. Small amounts of hydrolyzates (clay) and oxidates (ferric oxide) usually accompany the evaporates.

During the concentration of sea water by prolonged evaporation, the salts dissolved therein will crystallize in the reverse order of their solubility, the least soluble salts separating first. However, it must be noted that the dissolved constituents rather strongly affect one another's solubility, and therefore the course of crystallization of the salts is complicated. Jacobus Hendrikus van't Hoff (1852-1911), the Dutch chemist, carried out extensive and detailed research on the crystallization of the salts and the metamorphic processes connected therewith. His and later studies showed that, during the concentration of the brine, calcium carbonate precipitates first. Next calcium sulfate as gypsum and anhydrite will crystallize, followed by sodium chloride and, finally, under favorable conditions, the readily soluble potassium and magnesium salts will separate. The salt-mineral parageneses of the Stassfurt deposits are now interpreted as being produced by chemical reactions which took place during the burial of the beds to a depth of several kilometers and during the subsequent uplifting. Temperatures as high as 170° C. may have prevailed during the burial.

The evaporates from closed basins are known both in the ancient sediment columns and among the recent deposits of semiarid and arid regions. These deposits show rather pronounced local changes, as far as their chemical and petrological properties are concerned. Their character depends essentially on their geological environments. The salts are derived from the surrounding rocks and are transported into the closed basins by surface waters. The evaporates formed consist predominantly of sulfates, carbonates, or chlorides, though borates

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may also be present. Sodium, sometimes with calcium, predominates among the cations; but the content of potassium and magnesium, the metals characterizing marine evaporates, is conspicuously low. Sodium sulfate is deposited in notable quantities in many salt lakes. If the surrounding geological complexes consist of sedimentary rocks which contain salt deposits, sulfates and chlorides predominate in the evap-

TABLE 5.50
ANALYSES OF EVAPORATES
(Composition Given in Per Cent by Weight)

Constituent	Rock Salt, Katwee Lake, North of Albert Edward Nyanza, Central Africa	Rock Salt, Goderich, Canada	Sodium Sulfate, Center of Sevier Lake, Utah, U.S.A.	Incrustation from Alkaline Lake, near Peko Station on Humboldt River, Nev., U.S.A.	Caliche, Atacama Desert, North Chile
NaCl.	82 71	99 687	7 0	7 24	27 55
CaCl ₂	n.d.	0 032	n.d.	n.d.	n.d.
MgCl ₂	n.d.	0 095	n.d.	n.d.	n.d.
Na ₂ SO ₄	5 32	n.d.	84 6	4 42	2 13
K ₂ SO ₄	8 43	n.d.	n.d.	n.d.	n.d.
CaSO ₄	n.d.	0 090	trace	n.d.	0 41
MgSO ₄	n.d.	n.d.	trace	n.d.	0 15
Na ₂ CO ₃	2 46	n.d.	0 4	48 99	n.d.
NaHCO ₃	n.d.	n.d.	n.d.	36 01	n.d.
Na ₂ B ₄ O ₇	n.d.	n.d.	n.d.	3 34	0 43
NaNO ₃	n.d.	n.d.	n.d.	n.d.	61 97
KNO ₃	n.d.	n.d.	n.d.	n.d.	5 15
NaIO ₃	n.d.	n.d.	n.d.	n.d.	0 94
Na ₂ CrO ₄	n.d.	n.d.	n.d.	n.d.	trace
KClO ₄	n.d.	n.d.	n.d.	n.d.	0 21
NH ₄ salts	n.d.	n.d.	n.d.	n.d.	trace
Fe ₂ O ₃	0 15	n.d.	n.d.	n.d.	n.d.
H ₂ O	0 82	0 079	8 0	n.d.	0 67
Insoluble.	n.d.	0 017	trace	n.d.	0 39
Total	99 89	100 000	100 0	100 00	100 00

orates of the region. In areas consisting of igneous and metamorphic rocks the evaporates often contain carbonates as predominating constituents.

The evaporates at least partly connected with volcanic emanations and released in hot springs include borate deposits, but the majority of these deposits are formed by a precipitation process which is not caused by extensive evaporation of the solvent. Consequently, they are precipitates.

The evaporates consisting predominantly of nitrates are rare and evidently require singular conditions of formation. They may form

under the action of micro-organisms and subsequently collect into separate beds in arid regions. Nitrate deposits, e.g., those of Chile, often carry considerable amounts of iodine, chiefly as iodate.

The chemical composition of some evaporates is presented in Table 5.50, which is based on analyses collected and published by Clarke (1924).

TOTAL QUANTITY OF THE SEDIMENTS

The knowledge of the total amount of sediments formed on the Earth since the beginning of the processes of weathering, transportation, and deposition is of high geochemical importance. In a similar manner it is important to know the total quantity of igneous and other rocks decomposed during the geological evolution. Some estimates of the amount of weathered rocks and of the amount of the sediments formed therefrom have been based on the measurement of the total thickness of sediment beds formed in the different parts of the Earth during different geological periods. Inasmuch as the geological column nowhere contains a continuous series of all sediments, such estimates have yielded rather questionable results. The calculations based on certain facts pertaining to the chemical composition of sea water and of various sediments, on the other hand, give results of a more satisfactory character.

Complete calculations of the total amount of sediments were published by Goldschmidt (1933a). The average composition of argillaceous sediments, with few exceptions, is rather similar to the average composition of igneous rocks (see Table 5.51). Goldschmidt calculated the amount of weathered igneous rocks and that of the sediments formed therefrom on the basis on the sodium content of sea water. The total amount of sea water is about 278 kg for every square centimeter of the Earth's surface (see chap. 6), and this quantity contains 2.975 kg Na. The average content of sodium in igneous rocks, as given in Table 2.2, is 2.83 per cent Na. The sodium content of argillaceous sediments may be derived from a number of composite analyses, which are presented, according to Goldschmidt (1933a), in Table 5.51. The analyses of shales and muds are from Clarke (1924).

A chemical comparison of igneous rocks with argillaceous sediments reveals that the argillaceous sediments, on an average, contain less MgO, CaO, and Na₂O and more K₂O and CO₂ + C + H₂O than do the igneous rocks. If the sodium content is calculated, it is found that the typical argillaceous sediments contain about 1 per cent Na.

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The analyses quoted in Table 5.51 show that the following changes take place when argillaceous (and arenaceous) sediments are formed from the material of igneous rocks: the content of CaO (calculated for an argillaceous sediment free of carbonates and with 0.6 per cent CaO) decreases by about 4.5 per cent; the content of MgO decreases by 1.0 per cent; and the content of Na₂O decreases by 2.5 per cent. Consequently, the total decrease is 8 per cent. It is partly compen-

TABLE 5.51

AVERAGE CHEMICAL COMPOSITION OF IGNEOUS ROCKS COMPARED WITH COMPOSITION OF SOME ARGILLACEOUS SEDIMENTS
(Partial Analyses, Composition Given in Per Cent by Weight)

Constituent	Igneous Rocks	Composite of 78 Shales	Composite of 52 Terrigenous Muds	Composite of 18 Phyllites, Stavanger Area, Norway	Composite of 11 Phyllites, Central Norway	Composite of 12 Phyllites, Central Norway	Composite of 30 Garnetiferous Mica Schists, Trondheim Area, Norway	Composite of 11 Stauro-lite-bearing Mica Schists, Trondheim Area, Norway
SiO ₂	59.12	58.38	57.05	57.29	63.09	65.10	67.34	61.25
Al ₂ O ₃	15.34	15.47	17.22	20.00	16.70	14.92	13.78	17.26
FeO*	6.57	6.07	6.86	6.79	6.16	5.84	6.37	7.62
MgO	3.49	2.45	2.17	1.76	2.43	2.23	3.05	4.83
CaO	5.08	3.12	2.04	0.37	0.40	1.11	1.38	1.05
Na ₂ O	3.84	1.31	1.05	1.40	1.32	0.98	1.31	1.35
K ₂ O	3.13	3.25	2.25	4.30	4.59	4.82	3.34	3.22
H ₂ O	1.15	5.02	7.17					
CO ₂	0.10	2.64	n.d.	0.05	trace	0.65	0.10	0.30
Total	97.82	97.71	95.81	91.96	94.69	95.65	96.67	96.88
H ₂ O+CO ₂ +C.	1.25	8.47	8.86	4.91	4.05	3.74	2.08	2.46

* Total iron as FeO.

sated for by the increase in water content, which for unmetamorphosed shales amounts to about 5 per cent. Therefore, the total loss is about 3 per cent, and if X designates the total quantity of the weathered igneous rocks and Y the amount of the argillaceous (and arenaceous) sediments so far formed, both X and Y being expressed in kg·cm⁻², it follows that

$$Y = 0.97 X.$$

From the sodium content of sea water, 2.975 kg·cm⁻² Na, and that of the argillaceous sediments, 1 kg·cm⁻² Na, the following equation is derived:

$$2.83X - Y = 100 \cdot 2.975.$$

The two equations give

$$X = 160, \quad Y = 155.$$

In other words, 160 kg·cm⁻² igneous rocks have yielded by weathering 155 kg·cm⁻² argillaceous and arenaceous sediments.

This calculation, of course, gives only an approximate estimate. Neither the amount of the sodium-rich evaporates that have crystallized from sea water is considered nor the quantity of sodium delivered into the sea by volcanic emanations and juvenile waters. Moreover, the calculation is based on the assumption that all sodium found in the sea today has been produced by weathering and that no sodium was present in the primordial hydrosphere, which was formed by the condensation of atmospheric water vapor. Further, the amount of sodium retained in the resistates has not been considered in the calculation.

Goldschmidt's (1933a) calculations of the total amount of calcitic and dolomitic limestones are based on the following data:

The content of calcium in 278 kg sea water is 0.117 kg Ca, and the content of magnesium therein is 0.361 kg Mg. The CaO content of igneous rocks and of arenaceous and argillaceous sediments (carbonates excluded) is 5.08 and 0.6 per cent, respectively. The corresponding MgO contents are 3.49 and 2.6 per cent. The content of calcium and magnesium in 160 kg igneous rocks is 8.128 kg CaO and 5.584 kg MgO; in 155 kg arenaceous and argillaceous sediments, 0.930 kg CaO and 4.030 kg MgO; and in 278 kg sea water, 0.164 kg CaO and 0.598 kg MgO.

The calculations show that 7.034 kg CaO and 5.519 kg CO₂, or a total of 12.553 kg CaCO₃, is present in sedimentary rocks. For MgO, CO₂, and MgCO₃, respectively, the figures are 0.956, 1.043, and 1.999 kg. The quantity of dolomite, CaMg[CO₃]₂, that corresponds to 1.999 kg MgCO₃ is 4.372 kg, and consequently the amount of CaCO₃ is reduced to 10.170 kg. The compiled results are shown in the accompanying tabulation. These values are, according to Goldschmidt,

Sediment	Quantity (kg·cm ⁻²)	Specific Gravity (g·cm ⁻³)	Thickness of Deposits (m)
Shales and sandstones.....	155	2.65	585
Calcitic limestones.....	10.2	2.7	38
Dolomitic limestones.....	4.4	2.9	16
Total.....	169.6		639

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maximum values. The components never occur in a pure state in Nature, and, even though this fact does not affect the calculated total quantity, it affects the quantities of the various sediments. The calculation shows that, at any rate, the amount of the carbonate sediments is only one-tenth the amount of the arenaceous and argillaceous sediments.

The total volume of the sediments on the Earth, calculated from Goldschmidt's value of $155 \text{ kg} \cdot \text{cm}^{-2}$ for the arenaceous and argillaceous sediments, is about $3 \cdot 10^8 \text{ km}^3$. Clarke (1924) found 84,300,000 cubic miles, or about $3.5 \cdot 10^8 \text{ km}^3$ as the highest possible value of the volume of decomposed igneous rocks. Kuenen (1941) concluded that these values were too low and suggested a new value, approximately $13 \cdot 10^8 \text{ km}^3$. According to Kuenen, the total thickness of all sediments, including pore space, averages 3,000 m. Kuenen's value is based on the rate of deposition of sediments on the ocean bottom. However, Kuenen (1946) later revised his value once more, accepting the value $7 \cdot 10^8 \text{ km}^3$ as the outcome of geochemical calculations for all sedimentary material. The continental sediments are of the order of $2 \cdot 10^8 \text{ km}^3$, and, consequently, the value for the deep-sea deposits is $5 \cdot 10^8 \text{ km}^3$. Other determinations carried out by various methods give somewhat different values for the deep-sea deposits, but all the values are of the same degree of magnitude. Consequently, Goldschmidt's value may well be used as the basis of geochemical calculations, but the possibility must be considered that the amount of sediments actually is greater than his calculations indicate, and therefore a correction should be introduced into the quantitative treatment of the geochemical cycles of the elements.

A rough estimate of Holmes (1947) gives for the total maximum thickness of sediments accumulated during the whole of the geological time, i.e., in about 3,000 million years, the value 459 km.

CHEMICAL DIFFERENTIATION DURING SEDIMENTATION

A pronounced chemical differentiation takes place during the crystallization of magmas and leads to the formation of igneous rocks with different bulk composition. The differentiation is affected by a number of forces and phenomena and may in special cases develop complicated branches. It takes place deep under the Earth's surface and thus belongs to the group of endogenic phenomena. The processes connected therewith cause the endogenic differentiation of matter in Nature.

Another kind of chemical differentiation, called the exogenic differentiation of matter, takes place on the surface of the Earth. The exogenic differentiation is intimately connected with the minor cycle of matter. The geochemical classification of the sediments presented and discussed in the foregoing paragraphs is based on the characteristics of processes that predominate in the formation of the sediments. The differences in the manner of formation of the sediments cause a rather pronounced sorting of the elements into the various products of sedimentation. Some elements become strongly enriched in certain types of sediments, and for many elements the exogenic differentiation is the most powerful concentrating and enriching agent.

The Earth's surface may be considered a huge chemical laboratory, in which a quantitative rock analysis is being made. However, the results show that the method applied, viz., the exogenic differentiation, does not give fully satisfactory separation of the elements. The highest purity is obtained in the biogenic siliceous and calcareous sediments that may contain in excess of 90 per cent SiO_2 and CaCO_3 , respectively. Among the resistates the sandstones may contain up to 90 per cent SiO_2 . Iron and manganese are strongly enriched in the oxidates. As far as manganese is considered, magmatic processes seldom produce valuable manganese deposits, whereas manganese ores of sedimentary origin are numerous. In a similar manner the biggest iron-ore bodies in the world are sedimentogenic.

Some values to illustrate the sorting of the elements in the exogenic cycle are presented in Table 5.52, which is based on the average composition of igneous rocks given in Table 2.3 and on the average composition of resistates (sandstones), hydrolyzates (shales), and precipitates (limestones) given by Clarke (1924) according to H. N. Stokes's analyses (the main constituents and a number of trace elements). Most of the values for the trace elements are from original investigations on sediments, sedimentary rocks, and their metamorphosed derivatives quoted in Part II of this book. It must be strongly emphasized that the values given in Table 5.52 are still only tentative. Thus far, no average calculations at all have been presented for the oxidates and the evaporates. With particular reference to trace elements, Table 5.52 is far from complete. Even though the manner of distribution among the various groups of sediments is known for most trace elements, their average content in the sediments and in their derivatives is still very inadequately known.

TABLE 5.52

AVERAGE CHEMICAL COMPOSITION OF SEDIMENTARY ROCKS COMPARED
WITH AVERAGE COMPOSITION OF IGNEOUS ROCKS
(Composition Given in g/ton)

Element	Igneous Rocks	Sandstones, Etc	Shales, Etc.	Limestones
Li	65	17	46	>26
Be.....	6(?)	0	<3.6	0
B.....	3	9-31	310	3
C.....	320	13,800	15,300	113,500
F.....	600-900		510	250
Na.....	28,300	3,300	9,700	370
Mg.....	20,900	7,100	14,800	47,700
Al.....	81,300	25,300	81,900	4,300
Si.....	277,200	367,500	272,800	24,200
P.....	1,180	350	740	175
S.....	520	2,800	2,600	1,100
Cl.....	314	trace		200
K.....	25,900	11,000	27,000	2,700
Ca.....	36,300	39,500	22,300	304,500
Sc.....	5(?)	0.7	6.5	0
Ti.....	4,400	960	4,300	
V.....	150	20	120	<10
Cr.....	200	68-200	410-680	2
Mn.....	1,000	trace	620	385
Fe.....	50,000	9,900	47,300	4,000
Co.....	23	0	8	0
Ni.....	80	2-8	24	0
Cu.....	70		192	20.2
Zn.....	132	<20	200-1,000	≅50
Ga.....	15(?)	7.4	50	≅3.7
Ge.....	7(?)	3	7	
As.....	5		~5	
Se.....	0.09		0.6	<0.1
Br.....	1.62		>0.2	
Rb.....	310	273	300	0
Sr.....	300	<26	170	425-765
Y.....	28.1(?)	1.6	28.1	0
Zr.....	220		120	
Ag.....	0.10	0.44	0.05	0.2
Cd.....	0.15	0	0.3	
In.....	0.1	0.3	0.5	
Sn.....	40		40	
Sb.....	1	1	3	
I.....	0.3			0.07-0.55
Cs.....	7		12	
Ba.....	250	170	460	120
W.....	1.5-69		1-2	
Re.....	0.001	<0.001	<0.001	
Au.....	0.005	0.028		0.005-0.009
Hg.....	0.077-0.5	0.1	0.3	0.03
Tl.....	0.3-3	2	2	
Pb.....	16	20	20	5-10
Bi.....	0.2	0.3	1	
Ra.....	1.3·10 ⁻⁶	0.71·10 ⁻⁶	1.08·10 ⁻⁶	0.42·10 ⁻⁶
Th.....	11.5(?)	6.1	10.1	1.1
U.....	4	1.2	1.2	1.3

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Table 5.52 shows that some elements become enriched in certain groups of sediments, even though a high degree of separation is not always reached. Silicon and zirconium are concentrated in sandstones. Aluminum, iron, potassium, barium, thorium, and boron, among others, become enriched in the shales. Calcium, magnesium, and carbon concentrate in limestones. Along with iron and manganese, elements like barium, cobalt, and arsenic become concentrated in the oxidates. The elements that form readily soluble compounds remain in sea water and finally become concentrated in the evaporates. This group includes sodium, chlorine, and also potassium, magnesium, and sulfur.

ROLE OF HYDROGEN-ION CONCENTRATION IN GEOCHEMISTRY

Most of the phenomena of the minor cycle are characterized by the presence of water. Consequently, the physicochemical properties of water must be factors of decisive importance for the exogenic differentiation of matter. In a similar manner, they are important during the last stages of magmatic differentiation, viz., crystallization from

TABLE 5.53
VALUES OF pH IN NATURAL WATERS

Water	pH
Crater lake water, Java (H_2SO_4 present)	1.5
Peat water	4-4.5
Rain in open country	5.9
Moorland stream	6.4
Springs in calcareous regions	6.0-6.6
Lake and river water, noncalcareous	6.5-7.0
Lake and river water, calcareous	8.0-8.4
Ponds with weeds (active photosynthesis)	9.6
Sea water on the surface	8.1-8.4
Sea water in pools (active photosynthesis)	8.6
Sea water, depth of 1,000 m, Black Sea (H_2S present)	7.26
Water in alkali soil, Sudan (Na_2CO_3 present)	10.0

hydrothermal solutions. As a matter of fact, it is often hard to decide where the action of the magmatic phase ends and the action of surface waters begins, e.g., when dealing with phenomena of declining volcanic activity.

Among the physicochemical properties of water, its solvent action is geochemically of foremost importance. The solution processes are connected with electrolytic dissociation, whereby electrically charged ions are produced. The hydrogen-ion concentration of aqueous solutions is also of importance in geochemistry, as Atkins (1930) first pointed out. He gave the values for the pH of natural waters reproduced in Table 5.53.

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The great majority of natural waters has a pH between 6 and 8. The lowest pH reported, -1, was found in a desert soil containing free sulfuric acid.

The pH in soil is usually 2-12, but most soils are neutral in reaction. In peat soils the pH varies between 4.4 and 7.3 and in mineral soils between 4.8 and 8.2. The pH of soil regulates the metal uptake of plants by affecting the solubility of salts in soil solutions; but other factors also are effective as regulating agents.

Dissolved carbon dioxide is important in regulating the pH of waters. Photosynthesis tends to increase the pH of water, owing to the consumption of the carbon dioxide. Limestone beds may regulate

TABLE 5.54
VALUES OF pH FOR PRECIPITATION
OF HYDROXIDES
(Initial Precipitation)

Ion	pH
Fe ³⁺	3
Zr ⁴⁺	3
Sn ²⁺	3
Th ⁴⁺	3.5
Al ³⁺	5
Fe ²⁺	5 1
Cr ³⁺	5.5
Zn ²⁺	6
Mn ²⁺	8
Mg ²⁺	10
Ca ²⁺	11

the pH of circulating pore solutions. Many deposits of zinc and other metals are the result of the neutralizing action of limestone on acid hydrothermal solutions until the pH of precipitation of zinc sulfide is reached.

In the precipitation of hydroxides the pH plays an important role, even though it must be remembered that colloidal phenomena for some elements are still more decisive. Atkins (1930) gives pH values for the precipitation of some hydroxides as shown in Table 5.54. The precipitation of iron as ferrous hydroxide is not complete even in a neutral solution (pH 7). Therefore, ferrous compounds, under reducing conditions, may be transported in natural waters. Ferric salts may be transported only in very acid solutions, which are seldom present in Nature.

The precipitation of aluminum as hydroxide starts at pH 5, and heavy precipitation sets in at pH 6. Aluminum is stable both in acid and in alkaline solution. The great difference in the pre-

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precipitation of $\text{Fe}(\text{OH})_3$ and of $\text{Al}(\text{OH})_3$ is the cause of the separation of iron and aluminum during the exogenic cycle. Sometimes it may lead to the formation of pure deposits of aluminum hydroxide.

The solubility of silica also depends on the pH and increases parallel to increasing pH values.

Brucite, $\text{Mg}(\text{OH})_2$, evidently may precipitate only from strongly alkaline solutions.

The precipitation of sulfides depends on the pH, but the concentration of the S^{2-} and SH^- ions also affects the precipitation.

ROLE OF REDOX POTENTIAL IN GEOCHEMISTRY

Because many elements occur in Nature in two or more oxidation states, oxidation and reduction are geochemically important processes. Iron, which is geochemically the most important of all metals, is found in Nature in the oxidation states 0, 2, and 3, that is, as native metal, as ferrous, and as ferric compounds. The oxidation states for some other elements are the following:

Mn.	2, 3, 4
S	-2, 0, 6
V	3, 4, 5
Cu.	0, 1, 2
Pb.	0, 2, 4
N	-3, 0, 5
I.	-1, 0, 5

V. I. Vernadsky repeatedly emphasized the importance of atmospheric oxygen as an oxidizing agent in the exogenic cycle. Oxidation and reduction are of importance also in the first geochemical differentiation of terrestrial matter and during the crystallization of igneous rocks. However, the presence of molecular oxygen and of reducing material of organic origin in the exogenic cycle shows that here both oxidation and reduction occur in their geochemically most important surroundings.

The degree of oxidation and reduction is measured by means of the redox (O/R) potential, also called electrode potential, oxidation potential, reduction potential, and oxidation-reduction potential. The redox potential is the measure of the energy of oxidation or the electron-escaping tendency of a reversible oxidation-reduction system. It states how oxidizing or how reducing the system is with reference to the reaction



The redox potential of a system is referred to some other potential, commonly to the redox potential of the above reaction, which is ar-

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bitrarily fixed as zero. However, Goldschmidt (1943) emphasized that the redox potential varies notably in reactions in which one of the substances is a complex compound, e.g., a crystalline phase. Consequently, the values given for aqueous solutions are not directly applicable to reactions in which mineral phases participate.

The reducing power of a system increases with decreasing redox potential. The redox potential generally decreases with increasing temperature. Also the hydrogen-ion concentration affects the redox potential in so far as the latter generally decreases with increasing pH in an aqueous solution. On the other hand, the redox potential affects the pH as soon as notable amounts of material participate in reactions and no buffer substances are present.

The meteorites represent a considerably lower oxidation state than do terrestrial rocks, and their analyses show the preponderance of ferrous iron over ferric iron. Moreover, they contain native nickel-iron and meteorite minerals, such as oldhamite, CaS , which is unstable in the presence of water, and daubréelite, FeCr_2S_4 , which is unknown in terrestrial surroundings. The presence of much chromium, manganese, vanadium, and sometimes calcium in the sulfide phase of the meteorites characterizes their low redox potential.

Goldschmidt (1943) presented a discussion on the oxidation state of iron in igneous rocks, as represented by the atomic $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. The redox potential changes very regularly during differentiation. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is low in the early crystallates and increases strongly toward the late crystallized silicic rocks. In the essexite gabbros, which are the oldest intrusive rocks of the Oslo area in Norway, the ratio is 0.47, whereas the last granitic differentiates have a ratio of 2.4–2.7. In the effusive rocks the ratio is higher, starting with 1.4 in the essexite lavas and ending with 2.2 in the rhomb porphyries. In hypabyssal rocks the ratio is more variable and evidently is rather strongly affected by the chemical composition of the wall rock. According to Goldschmidt, the thermal changes of the equilibrium between Fe^{2+} and Fe^{3+} and those between water vapor and molecular hydrogen probably will largely determine the magnitude of the redox potential during differentiation.

On the Earth's surface the precipitation and mobilization of a number of elements in aqueous solutions depends on the pH. Along with the pH, the redox potential is of decisive importance, and the two functions together, especially the differences in redox potential, cause many highly important separation and enrichment processes,

which may result in the separation from one another even of chemically closely related elements, e.g., of sulfur and selenium, and in the formation of valuable ore deposits.

Iron, manganese, and cobalt are often precipitated as a result of oxidation reactions in the exogenic cycle. When bivalent iron and manganese are oxidized to the trivalent and quadrivalent states, respectively, they will precipitate as hydroxides even in relatively acid solution.

Numerous elements, such as sulfur, selenium, arsenic, chromium, vanadium, molybdenum, tungsten, and uranium, may be oxidized to readily soluble complex anions which are readily mobilized.

The redox potential of the environment is an important factor in the formation of minerals and in the concentration of certain elements in aqueous solutions. The occurrence of native elements which often form by precipitation from an aqueous solution is explained by the redox potential (Goldschmidt, 1933*b*; Chapman and Schweitzer, 1947). The higher the redox potential of a metal, the greater its tendency to occur in the native state.

A relatively high redox potential is essential to the formation of the vanadate minerals of lead, copper, zinc, and other metals that occur in sandstones (see chap. 25). The highest redox potential connected with the formation of minerals is found in the Chilean nitrate deposits in which perchlorates, iodates, and some chromates and selenates are present and even enriched (see chap. 23). This is the nitrate facies of Ščerbina (1939). These examples show that an unusually high redox potential may cause the enrichment of certain elements.

The elements may also become enriched under highly reducing conditions. A very low redox potential is maintained in rocks containing sulfides of heavy metals, e.g., of iron and copper. The weathering of such rocks may result in the formation of rich ore bodies in the zone of cementation, because iron remains, as oxide or hydroxide, in the region of high redox potential (in the oxidation zone), and the cupriferous solutions descend to areas of low redox potential below the water table and precipitate copper in the form of rich sulfide ores of univalent copper. Silver and other metals are often enriched along with copper. In coal and petroleum deposits the redox potential is very low and causes the enrichment of many rare elements. The occurrence of rare elements in coal and petroleum ashes is discussed in chapter 8. The concentration of the minor constituents in the bioliths has taken place in the original reducing environments, such as

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marine muds and decaying vegetable remains. The high adsorptive capacity of the carbonaceous matter has further facilitated the precipitation of the elements.

Biochemical processes often participate in the production of oxidizing or reducing environments. They may even dominate therein. When green plants synthesize organic compounds, molecular oxygen is liberated. It is responsible for the high redox potential on the Earth's surface. On the other hand, the organic matter, during its decay, creates very low redox potentials. The principal gaseous products of the bacterial decomposition of organic matter in a reducing environment are hydrogen, hydrogen sulfide, methane, and possibly other volatile hydrocarbons. Only little carbon dioxide is formed. The reducing conditions are maintained by the presence of certain organic and inorganic compounds, e.g., sulfoproteins, ferrous iron, manganous manganese, and hydrogen sulfide. Therefore, the conditions favor the hydrogenation of organic matter and the formation and preservation of petroleum hydrocarbons. Under oxidizing conditions, on the other hand, the micro-organisms tend to carbonize organic matter, the last stage of the process being the formation of coal, or to oxidize it to carbon dioxide. According to ZoBell (1946*b*), positive values of redox potential are generally characteristic of well-aerated marine sediments, those which are coarse grained, and those which are poor in organic matter. Negative values characterize fine-grained sediments and those rich in organic matter.

During the minor cycle the two extremes of redox potential are represented by the resistates, which have high redox potentials, and by the bituminous sediments and their derivatives, in which the redox potential tends to be particularly low.

During weak metamorphism the degree of oxidation, according to Goldschmidt (1943), often remains unchanged. Thus, e.g., newly formed hydrothermal hematite may be present in veins of metamorphosed granites, whereas less oxidized rocks, such as phyllites and metamorphosed gabbros, contain magnetite and siderite.

In many metamorphic rocks the high degree of oxidation may afford proof of their superficial origin, e.g., in certain ferriferous mica schists which originally were limonite- and hematite-bearing argillaceous sediments. It is evident that, once oxidized, rocks tend to retain their oxygen during metamorphism. However, reduction will gradually take place, and it proceeds through anatexis and palingenesis, which lead back to a rock melt.

ROLE OF SORPTION IN GEOCHEMISTRY

The ionic properties of an element, along with its affinity relationships, determine its manner of occurrence in the crystalline phases (rocks and their minerals) in Nature. During the weathering, a part of the chemically decomposed material goes into solution, partly as ions and partly as colloidal particles. In rivers, lakes, and, in particular, the sea, both ions and colloids succumb to a number of reactions which cause the distribution of the elements between the solid phase (sediments) and the liquid phase (water). The ionic properties of the elements largely regulate the distribution, but the properties of the colloidal particles or the ultramicros must also be considered. A group of phenomena which may be called geochemical sorption is of high importance for the properties of colloidal sediment particles and for the distribution of the elements among the various sediments (Noll, 1931). The following processes are of importance for the geochemistry of sediments of colloidal origin:

1. Precipitation of dissolved colloids
2. Flocculation of colloids by the action of electrolytes
3. Flocculation of colloids by the mutual action of oppositely charged sols
4. Ionic sorption and base exchange

The precipitation of colloids depends on the pH of the solution and on the redox potential. The other processes are governed by sorption.

Sorption takes place when ions or colloidal particles from either one of two phases are taken up at the phase boundary. Geochemically, sorption is characteristic of the natural colloidal phases. In natural waters, particularly in the sea, the attraction will occur at the boundary between the liquid and the solid phase. The adhesion either is adsorption, a purely physical surface attraction, or chemisorption, in which case the attracted particle will react chemically with the adsorbent. Usually the two kinds of sorption co-operate, and numerous intermediate stages exist between the two extremes. The sorption of ions by colloidal particles is the most important sorption phenomenon in Nature. The sorption on an amorphous gel is considerably stronger than sorption on a crystalline particle.

Like ions, the colloidal particles are electrically charged. Their charge is caused either by the partial dissociation of their superficial parts or by the sorption of ions from the surrounding solution on

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their surface. The charged particle is surrounded by an adsorbed electric layer that attracts ions with an opposite charge from the solution. The ions form a readily mobile cloud of changing thickness and density, which follows the particle in its movements. The electric system thus formed resembles, in its simplest form, a spherical condenser with the electrokinetic potential

$$\zeta = \frac{e\delta}{Dr(r + \delta)},$$

where e is the charge of the particle, r the radius of the charged particle and of the surrounding ion cloud (they are approximately of the same magnitude), δ the distance between the surface of the charged particle and the surface of the ion cloud, i.e., the thickness of the electric "atmosphere" or ion cloud, and D the dielectric constant of the surrounding medium. ζ is called the zeta potential or the tangential potential difference.

If a solution contains suspended particles with charges that are of equal magnitude and of the same sign and if the zeta potential of the particles is relatively high, the repulsive force between the approaching particles in the Brownian movement is strong enough to prevent the action of the attractive force between the molecules. In this case the sol is stable and cannot coagulate. If, on the other hand, the potential decreases below a critical value, the repulsive force between the sol particles is too weak to prevent the coagulation of the sol, i.e., the aggregation of the colloidal particles. Consequently, the magnitude of the zeta potential may be used to measure the stability of the colloidal solution. The flocculating power of an ion in a solution containing colloidal particles is directly proportional to its adsorptive capacity.

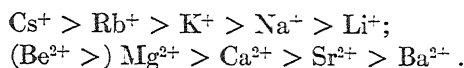
The sign of the electric charge of colloidal particles depends on the circumstances prevailing during their formation. Certain sols may obtain positive or negative charge according to the reactions in which they are formed. The sign of the charge of the geochemically most important sols in reactions taking place in Nature during the formation of argillaceous sediments is given in Table 5.55.

Noll (1931) listed several factors which govern the adsorptive capacity of ions. Ions present simultaneously in a solution will cause a decrease in the adsorbability of one another. The adsorptive capacity increases with increasing ionic charge. The smaller the radius of an ion in aqueous solution (hydrated radius), the greater its coagulation

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capacity and adsorptive capacity. Moreover, the adsorbability changes in conformity with polarizability, perhaps also parallel to increasing polarizing power and polar nature.

According to these rules such elements become relatively enriched in argillaceous sediments that are characterized by high attraction intensity, i.e., by low hydration and high polarizability, or by their property of forming sparingly soluble compounds with the sorbent. The order of decreasing enrichment is the following:



The argillaceous sediments are characterized by the fact that their K_2O content is higher than their Na_2O content. Moreover, their MgO

TABLE 5.55
ELECTRIC CHARGE OF SOLS OCCURRING IN NATURE

Positive	Negative
Aluminum hydroxide	Silica
Ferric hydroxide	Ferric hydroxide
Chromic hydroxide	Hydrate of vanadium pentoxide
Hydrate of titanium dioxide	Hydrate of manganese dioxide
Hydrate of zirconium dioxide	Humic colloids
Hydrate of thorium dioxide	Metal hydrosols
	Sulfide hydrosols

content is usually higher than their CaO content, whereas in river water Na_2O is higher than K_2O , and CaO higher than MgO . The explanation is the preferential sorption of potassium and magnesium in clays. The high content of copper, zinc, and lead in oceanic sediments may also be explained by adsorption. However, chemisorption may also be active, e.g., in the sorption of the phosphate anion by ferric hydroxide gels.

The neutralization of the electric charge is the common cause of the flocculation of a sol. The neutralization may be due to the action of ions, in which case it depends on their concentration and their adsorbability, or to the formation of a sparingly soluble precipitate by chemisorption. The neutralization may also result from the presence of an oppositely charged colloid. This phenomenon predominates in the formation of argillaceous sediments, and in the diluted solutions found in Nature it takes place prior to the flocculation by electrolytes. Whether a sol is flocculated completely or not depends on the pH and temperature of the solution.

Silica nearly always preponderates over other colloids in Nature.

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This fact is very important if the ions dissolved in natural waters are considered. The silica gel deposited in clays causes an excess of negative charge therein. The result is that the anions present in solution usually cannot become adsorbed in argillaceous sediments. The cations, on the contrary, are readily adsorbed in clays. In the laterites and bauxites, in which the positively charged aluminum hydroxide predominates, the adsorption of cations is rather weak. The precipitation of ferric hydroxide, according to its colloidal properties, may be the result of the mutual flocculation of oppositely charged ferric hydroxide sols.

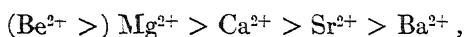
The protective action of certain substances on a colloid is caused by the privileged sorption of ions, molecules, or colloidal particles. This phenomenon is of high importance in the cycle of some elements, e.g., of iron, which remains in solution as colloidal ferric hydroxide because of the protective action of humic substances.

The potential is important also for the behavior of ions. The importance of ionic potential in physical chemistry was emphasized by Cartledge (1928). The ionic potential (Φ) is found by dividing the ionic charge (Z) by ionic radius (r):

$$\Phi = \frac{Z}{r}.$$

The potentials of some geochemically important ions are presented in Table 5.56.

Goldschmidt (1934, 1937a) showed that a number of phenomena connected with the distribution of elements between sea water and the sediments may be explained by considering the ionic potential of the elements in question. With reference to the distribution of the alkali metals, it is known that the bulk of sodium present in the weathering solutions is carried into the sea, whereas potassium is preferentially adsorbed in argillaceous sediments. Table 5.56 shows that the behavior of sodium and potassium is in accordance with their ionic potential. The metal with the lower ionic potential becomes adsorbed, but the metal with the higher ionic potential remains in solution. The heavy alkali metals, rubidium and cesium, are adsorbed in clays still more completely than potassium is, and Table 5.56 shows that their ionic potentials are lower than the ionic potential of potassium. The order of the relative enrichment of some bivalent cations in clays,



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shows a similar relationship and agrees completely with the order of decrease of the ionic potential (Noll, 1931). Also the other properties of ions and colloids discussed above, according to Noll, strongly affect the degree of adsorption of the ions by sediments.

However, Ross (1943) explained the preferential fixation of potassium in the hydrolyzates by the observation that montmorillonite will gradually invert to illite or mica-like minerals. The structures of

TABLE 5.56
VALUE OF IONIC POTENTIAL

Ion	Φ
Cs ⁺	0.61
Rb ⁺	0.67
K ⁺	0.75
Na ⁺	1.02
Li ⁺	1.38
Ba ²⁺	1.40
Sr ²⁺	1.57
Ca ²⁺	1.89
La ³⁺	2.46
Mg ²⁺	2.56
Sm ³⁺	2.65
Y ³⁺	2.83
Lu ³⁺	3.03
Sc ³⁺	3.61
Th ⁴⁺	3.64
Ce ⁴⁺	3.92
Zr ⁴⁺	4.60
Al ³⁺	5.26
Be ²⁺	5.88
Ti ⁴⁺	6.25
Cb ⁵⁺	7.25
Mo ⁶⁺	~9.7
P ⁵⁺	14.29
B ³⁺	~15
S ⁶⁺	17.65
C ⁴⁺	~26.7
N ⁵⁺	33.33

the micas and of montmorillonite are very similar, except that the K⁺ ions in the micas are between the sheets and are irreplaceable. In montmorillonite, Na⁺ and Ca²⁺ are readily replaced, whereas K⁺ gradually becomes irreplaceable. Therefore, potassium in favorable conditions may link the structural sheets together and consequently occupies positions similar to those of the K⁺ ions in the mica structure. Such potassium is rendered immobile.

Goldschmidt (1934, 1937a) divided the elements, on the basis of their ionic potential, into three groups, which become separated from one another during sedimentation in the sea. The division for a number of geochemically important cations is presented in Figure 5.19,

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which is based on the distribution diagrams given by Goldschmidt (1934, 1937*a*), with revisions according to Wickman (1944). Group I includes the cations that have low ionic potential. With certain exceptions, they remain in ionic solution even up to high values of pH. The cations belonging to Group II have a higher ionic potential than those of Group I. They are readily hydrolyzed and precipitate in the form of hydroxides, which are deposited among the hydrolyzates, e.g., beryllium, aluminum, titanium, columbium, zirconium, and thorium. Group III consists of ions with the highest potentials. They

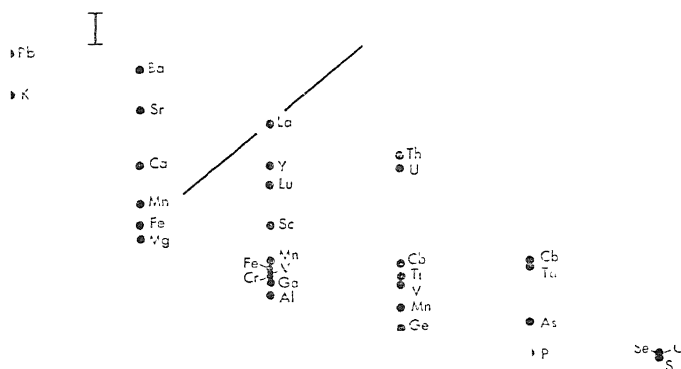


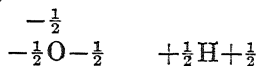
FIG. 5.19.—Geochemical division of some important elements on the basis of their ionic potential. *Abscissa*, charge of the ion. *Ordinate*, ionic radius in kX.

form complex anions with oxygen, which usually remain in ionic solution. Nitrogen, carbon, sulfur, and phosphorus belong to this group. They are present in sea water in the form of the complex anions NO_3^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} .

Goldschmidt (1934), however, remarked that the concept of the ionic potential is somewhat obscure. Evidently the ionic potential does not possess any immediate physical significance, and consequently the division presented in Figure 5.19 is only empirical.

Wickman (1944) gave a physical explanation of the empirical threefold grouping of the elements by substituting the concept of the ionic potential by the rules governing the hydrogen and hydroxyl bond in hydroxides. His results showed that the distribution of the elements between sea water and the hydrolyzates depends on the crystal structure of their hydroxides. Wickman based his treatment on

the interpretation of the hydrogen and hydroxyl bonds presented by Bernal and Megaw (1935), who showed that the role of hydrogen in hydroxides depends on the size of the cation and on its polarizing power. The OH^- ion bound to a cation is more or less polarized. If an increasing and divergent electric field is applied to the OH^- ion, it may be expected to pass through three stages. In the first stage, when the polarization is small, the OH^- ion retains the original cylindrical polar symmetry which characterizes the free OH^- ion. The resulting bond is ionic. In the second stage, as the polarization increases, the bond from the hydrogen atom to the oxygen atom will become definitely directed, and the polarization by the cation breaks the binegative oxygen ion into four concentrations of negative charge in a tetrahedral formation; each of the parts has the charge of $\frac{1}{2}$ unit. The structure of the OH^- group, presented schematically in terms of electrostatic valence, is



One of the negative halves of charge of oxygen is occupied by the hydrogen ion and gives a net charge of $+\frac{1}{2}$. There remain, consequently, four halves of charge, three of which are negative and one positive. Each of these charges is potentially a directed bond. The negative charge of oxygen in one hydroxyl group will attract the positive charge of hydrogen belonging to a neighboring hydroxyl group, and thereby a bond results that is called the hydroxyl bond. With further increase in polarization, the strength of the bond between the hydrogen ion and the oxygen ion will decrease, and in this case the hydrogen ion may be considered to belong to a neighboring oxygen, if there is one present, and hydrogen behaves in the structure like a free H^+ ion in 2-co-ordination, equidistant from the two O^{2-} ions: there exists a hydrogen bond.

If the electrostatic valence from the polarizing cation to the hydroxyl group is less than $\frac{1}{2}$, the charge of the oxygen ion will not show any tetrahedral splitting. Ionic bond is formed, and the hydroxide is readily soluble. If the electrostatic valence is $\frac{1}{2}$, one of the negative half-charges of oxygen will be occupied; and if the electrostatic valence is 1, two halves of the negative charge are required to bind the hydroxyl group to the cation. In these cases there remain unattached negative charges, which form hydroxyl bonds with the positive charges. If the electrostatic valence is greater than 1, a hydrogen

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bond is formed which is weak enough to cause the formation of a soluble complex anion.

From the considerations presented above, Wickman (1944) deduced the following rules:

- If $V < \frac{1}{2}$, ionic bonds are formed;
- If $\frac{1}{2} \leq V \leq 1$, hydroxyl bonds are formed;
- If $V > 1$, hydrogen bonds are formed.

The electrostatic valence (V) is the charge of the cation (Q) divided by its co-ordination number (C):

$$V = \frac{Q}{C}.$$

These rules may be used to interpret Goldschmidt's empirical diagram and to give physical significance to it. The soluble cations of Group I are those having ionic bonds in their hydroxides. The hydroxides of Group II, which are concentrated in the hydrolyzates, are characterized by hydroxyl bonds, and the complex anions of Group III have hydrogen bonds.

For univalent cations Q is 1. In order that their V should lie between $\frac{1}{2}$ and 1, the maximum value of C could be 2. However, in the hydroxides in question, C is always greater than 2, and therefore ionic bonds prevail therein. The univalent cations, consequently, belong to Group I of Figure 5.19.

The hydroxides of the bivalent cations usually have structures in which C of the cation is 1. Therefore, V is $\frac{2}{3}$ or $\frac{1}{2}$. These compounds have ionic bonds, are readily soluble, and belong to Group I. Beryllium, however, is an exception. Owing to its small size, the Be^{2+} ion is 4-co-ordinated in $\text{Be}(\text{OH})_2$, just as in the beryllium silicates. It follows that, for beryllium, V is $\frac{2}{4}$ or $\frac{1}{2}$, and thus beryllium hydroxide is insoluble and beryllium is an element of Group II. Zinc, according to Wickman (1944), lies on the boundary between the soluble cations and the hydrolyzates. Zn^{2+} may be both 4- and 6-co-ordinated in $\text{Zn}(\text{OH})_2$.

In order that trivalent cations may belong to Group I, they must, in their hydroxides, have C higher than 6. In the case of lanthanum this appears rather probable, but the structures of $\text{La}(\text{OH})_3$ and of the hydroxides of the trivalent lanthanides are still unknown. Aluminum, gallium, and ferric iron, on the other hand, are 6-co-ordinated in their hydroxides, e.g., in hydrargillite (gibbsite), $\gamma\text{-Al}(\text{OH})_3$; diaspore, $\alpha\text{-AlOOH}$; goethite, $\alpha\text{-FeOOH}$; and lepidocrocite, $\gamma\text{-FeOOH}$. Conse-

quently, they belong to Group II. They are, as a matter of fact, the most typical elements of the hydrolyzates. Boron is 3-co-ordinated in boric acid, H_3BO_3 or $\text{B}(\text{OH})_3$, and therefore its V is 1 and it belongs to Group II.

The quadrivalent cations, with the exception of carbon, always occur at least 4-co-ordinated but probably never have C higher than 8. Consequently, their V is equal to, or smaller than, 1, and they belong to Group II. Carbon, however, is typically 3-co-ordinated, and therefore hydrogen bonds prevail in the carbonate anion, and hence carbon belongs to Group III.

Among the quinquevalent ions nitrogen is 3- and phosphorus 4-co-ordinated. Therefore, they belong to Group III. In a similar manner, As^{5+} and V^{5+} may belong to Group III. However, the quinquevalent vanadium may lie on the boundary between Group II and Group III. Quinquevalent columbium and tantalum, on the other hand, probably are too large to be found in 4-co-ordination and consequently belong to Group II.

Among the sexvalent ions sulfur is 4-co-ordinated in the sulfate anion and therefore belongs to Group III. The Te^{6-} ion is 6-co-ordinated and consequently has hydroxyl bonds and must be expected to concentrate in the hydrolyzates.

The septemvalent ions probably belong to Group III.

Wickman's results on the distribution of elements between sea water and sediments refer only to their precipitation as hydroxides. It must be noticed that many cations of Group I are removed from sea water by sorption in argillaceous sediments (see Part II). Consequently, they are not removed solely by precipitation, and Wickman's explanation is not valid in such instances. With reference to Figure 5.19, it must also be emphasized that the boundary lines between the groups are to be regarded as narrow transition zones.

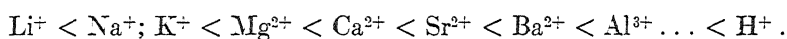
BASE-EXCHANGE CAPACITY OF CLAY MINERALS

Clay minerals are characterized by their property of carrying cations (anions) that may become exchanged for other cations (anions) present in aqueous solutions which are brought into contact with the clay material. This property is called the base-exchange capacity. It does not affect the structure of the clay minerals concerned. The mechanism of the anion exchange is almost entirely unknown, but extensive research has been carried out on the cation exchange. It is known that for certain clay minerals the base-exchange capacity

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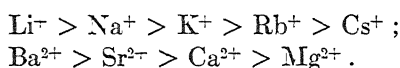
varies with the particle size; it is also related to crystal structure. In montmorillonite, most of the exchangeable ions (exchange positions) lie on the basal-plane surface; the rest are on the edges of the flakes. It has been suggested that the oxygen ions with incompletely satisfied valence bonds may hold the exchangeable ions at the flake edges and that the H^+ ion of the OH^- groups at flake edges may explain a part of the cation exchange. However, on the flake surfaces the exchange may result from the substitution of Al^{3+} by Mg^{2+} within the structure, whereby the charge necessary to retain the cations would be produced (Grim, 1942). In kaolinites a part of the exchange capacity may be caused by distortion of the structure. In illite much of the exchange capacity is found in the flake edges, but a part is due to substitutions within the structure.

The adsorbability series commonly adopted, in order of decreasing replaceability, is for some cations, according to Hauser (1939), the following:



This is the so-called Hofmeister series.

Noll (1931) gave the following series, in order of decreasing replaceability:



The replaceability is a function of ionic charge: the bivalent cations are more tightly held than the univalent cations. The replaceability depends also on the hydration and polarizability of the ions and on the solubility of the compounds that may form on the phase boundary. According to Page (quoted in Grim, 1942), the ionic size is important in the replacement, and ions fitting closely into the cavities within the hexagonal nets of O^{2-} ions are replaceable only with difficulty.

The relative exchangeability series is not valid for all clay minerals, but, instead, there is a series for each clay mineral. Ross (1943) gave the following series for the relative ease of replacement in montmorillonites:



This series indicates why calcium is preferentially fixed in most montmorillonites even in the presence of sodium.

THE MAJOR CYCLE AND ITS PRODUCTS

THE MAJOR CYCLE

The principles were presented in previous paragraphs, according to which the constituents of a rock melt separate to form various igneous rocks and other matter of juvenile origin. Moreover, the general principles were discussed that govern the disintegration of solid rocks and the formation of various sediments and sedimentary rocks. Attention was paid to the general geochemical mechanisms of the processes taking place in Nature and to the quality, quantity, and chemical composition of the products formed. The two series of phenomena connected with magmatic crystallization and with weathering and related processes cause an extensive and complicated chemical differentiation in the uppermost lithosphere and on the Earth's surface. In many instances the differentiation results in a pronounced sorting of the elements in the various products formed.

Both the primary igneous rocks and the sediments and their diagenetic products are formed by chemical differentiation. The differentiation phenomena evidently make up an essential part of all geochemical processes taking place in the uppermost geospheres. In the sense of Goldschmidt (1926, 1929, 1933*b*) these differentiation processes include the second stage of geochemical differentiation in the Earth, or the endogenic differentiation, and the third stage, or the exogenic differentiation (see chap. 10). In the uppermost lithosphere, however, processes of still another kind take place which cannot be included either in exogenic or in endogenic differentiation. Even though the processes of the third group in part tend to cause a chemical distribution of the elements among various rocks, they work essentially in the opposite direction, endeavoring to level off the chemical differences already produced. Contrary to the exogenic cycle, which takes place on the surface of the Earth, these processes occur at deeper levels in the crust. They form the endogenic cycle of matter. The endogenic and exogenic cycles together form the major cycle of matter.

The processes characterizing that part of the major cycle which, starting from sedimentary or igneous rocks, gradually produces a rock melt are geochemically as important as the phenomena of magmatic crystallization and of exogenic differentiation. The processes resulting in the re-fusion of rock material are largely, perhaps nearly entirely, based on reactions taking place in the solid state, and con-

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sequently they differ basically from the crystallization of melts and from the deposition of matter in aqueous solutions. It is possible that the migration of elements in the major cycle actually is the most important process in the chemical modeling of the upper lithosphere and that the schematic magmatic differentiation is only an idealized process. However, the present information available on the geochemistry of metamorphism is, at best, still very scarce and incomplete.

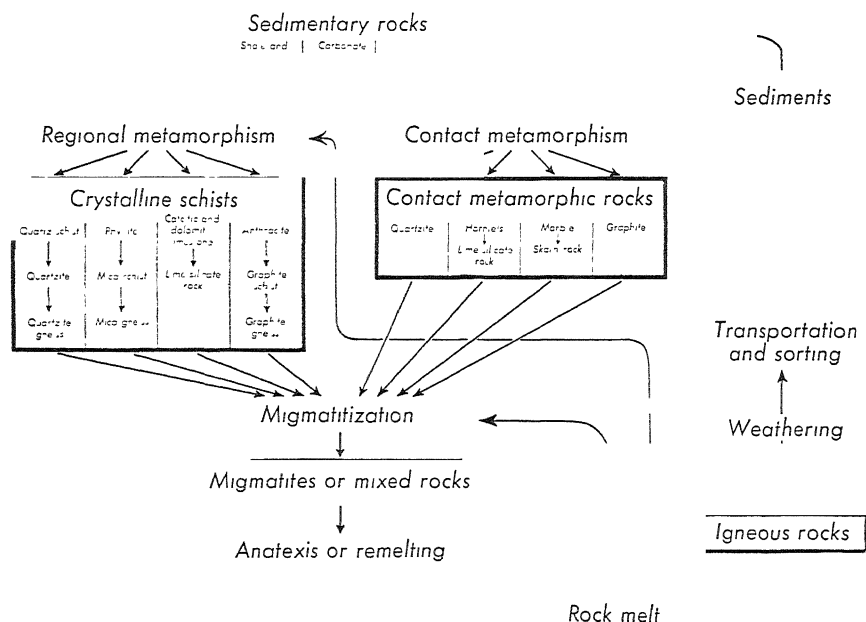


FIG. 5.20.—The major cycle

and many recent theoretical investigations, even those following closely related lines of reasoning, have produced contradictory results. Therefore, the discussion on the major cycle and on its products will be confined only to those processes that are of importance for the understanding of the general geochemistry of the upper lithosphere, and little attention will be paid to the structure and chemical composition of the various classes of metamorphic rocks.

Unlike the minor cycle, the major cycle is closed for all rocks participating therein. However, it must be noted that the hydrosphere, particularly the oceans, forms a considerable leak in the cycle. Numerous elements have collected in the water masses of the ocean basins at least semipermanently and have remained there for a very

considerable part of the Earth's geological history. In like manner the material deposited on the ocean bottom thus far has evidently not re-participated in the major cycle. Therefore, the major cycle is quantitatively deficient.

The course of the major cycle is presented in Figure 5.20. This figure shows that the cycle begins with molten rock and ultimately winds up with a regenerated rock melt. The melt, on cooling, will crystallize in the form of plutonic or volcanic rocks, depending on the level of the seat of crystallization in the lithosphere. The true igneous rocks, formed from a primary magmatic or juvenile material, must be distinguished from the quasi-igneous or pseudo-igneous rocks that are formed from or by a melt which is partly or totally a product of remelting. On the Earth's surface the igneous rocks participate in the minor cycle, and their material finally becomes distributed among the various sediments. Sedimentary rocks are formed by diagenesis from the sediments. Furthermore, the sedimentary rocks may re-participate in the minor cycle on the Earth's surface. However, the beds of sediments and of their derivatives may be removed from immediate contact with the hydrosphere and the atmosphere by continuing deposition of sediments or by tectonic movements. If that is the case, the sediments depart from the minor cycle and, in the course of time, they will participate in metamorphic processes.

METAMORPHIC CHANGES IN ROCKS

Metamorphism is the physical and chemical adjustment of rocks to conditions existing at the deeper levels of the upper lithosphere, below the zones of weathering and sedimentation. The metamorphic changes are essential for the endogenic processes that take place in the major cycle of matter. The field of metamorphism may be divided according to the nature of the primary metamorphic processes. In the classification presented by Turner (1948), the simple metamorphism is either purely mechanical (kinetic) metamorphism or purely thermal metamorphism, or metasomatism, which is the introduction and removal of material by magmatic gases (pneumatolytic metamorphism), solutions (hydrothermal metamorphism), or molten rock (migmatitization in part) and results in changes both in the mineralogy and in the chemistry of the rocks affected.

The field associations and the petrographic character of metamorphosed rocks may, in addition, give evidence of autometamorphism, which may or may not be accompanied by metasomatic changes.

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Autometamorphism consists of reactions between a rock and the residual solutions formed during the crystallization. Moreover, complex controlling conditions give rise, among others, to regional metamorphism over wide areas under the combined influence of elevated temperature, variable pressure, and high shearing stress and to plutonic metamorphism, which is the deep-seated regional metamorphism at high temperatures and pressures, often accompanied by strong deformation and augmented by injection and infiltration of molten rock or by incipient re-fusion. Regional metamorphism merges into plutonic metamorphism in the deep root zones of mountain chains, and still deeper the plutonic metamorphism merges into truly plutonic phenomena. In the shallow zones near the Earth's surface, regional metamorphism gradually becomes replaced by kinetic metamorphism. Deformation usually accompanies regional metamorphism at the lower levels in the crust and promotes and accelerates the incorporated chemical reactions.

During metamorphism the mineralogical and chemical composition of the rock is affected by changes in temperature, pressure, shearing stress, and chemical activity of the environment. Because the composition of the reacting system in metamorphism usually is complex, the chemical changes involved are also complicated. With changes in the environmental conditions, the minerals participating in metamorphic processes may become unstable, and their atoms and ions become rearranged into new structures which are, with reference to their stability and composition, adapted to the new conditions. With progressing regional metamorphism, the participating rocks often grow more coarse grained and appear more gneisslike. Migmatitization may set in with tectonic movements that promote the rate and extent of the metamorphic changes. The migration of the readily mobile elements, such as the alkali metals, begins, and the migrating materials collect into separate veins, thereby producing a veined gneiss (venite). Rocks of this kind may also form by the intrusion of molten rock material (arterites). The result of the migration and intrusion is the formation of migmatites, or mixed rocks, which are the predominating rocks in the deepest parts of mountain chains. A notable part of granites and associated rocks is believed to have formed by migmatitization (granitization). Because metamorphism may still increase in strength, it may lead to the partial remelting (anatexis) of the rock, later followed by a complete re-fusion. The remelt-

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ing consequently ends in the formation of a rock melt, the starting phase of the major cycle, and in its crystallization. The most far-reaching metamorphic changes, accordingly, mean the rebirth, or palingenesis, of the rock.

The argillaceous and arenaceous sediments are quantitatively the most important groups of sediments (see under "Total Quantity of

TABLE 5.57
CHEMICAL COMPOSITION OF SOME ARGILLACEOUS AND ARENACEOUS
SEDIMENTS AND OF THEIR METAMORPHIC DERIVATIVES
FROM FINLAND
(Composition Given in Per Cent by Weight)

Constituent	Late-Glacial Varved Clay, Dark Layer, Leppakoski	Varved Phyllite, Dark Layer, Ajonokka, Aitolahiti	Quartz Sand, Viasvesi	Quartzite, Tiirismaa, Lanti
SiO ₂	50 33	56.63	93.61	94 52
Al ₂ O ₃	19 17	22.41	2 69	2.38
Fe ₂ O ₃	6 50	0.58	0 09	0 84
FeO..... ..	2 52	5.05	n.d.	0 58
MnO..... ..	0 13	0.06	n.d.	0 05
MgO..... ..	3.77	2.35	0 05	0 04
CaO..... ..	1.43	1.28	0 64	0 00
Na ₂ O..... ..	1 78	2.31	0.70	0 16
K ₂ O..... ..	4.03	6.15	1.93	0 08
TiO ₂	1 13	1.04	n.d.	0 01
P ₂ O ₅	0.14	0.12	n.d.	n.d.
BaO..... ..	n.d.	0.05	n.d.	n.d.
H ₂ O..... ..	8 61	2.37	n.d.	1.36
S..... ..	n.d.	0.08	n.d.	n.d.
C..... ..	0.41*	0.31	n.d.	n.d.
Total	99 95	100.79	99.71	100.02

* Humic matter.

Sediments," p. 221). The argillaceous sediments are converted into hornfelses in thermal metamorphism and into various aluminum silicate gneisses, phyllites, and mica schists in regional metamorphism. The bulk chemical composition may thereby remain almost unchanged, as the analyses of Table 5.57 illustrate. The analyses are from Eskola (1932a) and Sederholm (1911). The increase in the K₂O content in the phyllite is caused by the metasomatic introduction of potassium. Table 5.57 also shows the composition of a quartz-rich sand (from Borgström, 1924), compared with the composition of a quartzite (from Eskola and Nieminen, 1938). Also in this case the similarity in chemical composition is fair.

METAMORPHISM AS A GEOCHEMICAL PHENOMENON

Metamorphic changes may affect any or all of the following properties of a rock: its fabric, its mineralogical composition, and its chemical composition. Strictly speaking, all physical and chemical changes in a rock, e.g., the crystallization of a rock melt, the weathering of rocks, and the deposition of sediments, should be called metamorphism. However, according to the current usage of the term, metamorphism includes only the structural, mineralogical, and chemical adjustments of solid rocks that take place in the endogenic phase of the major cycle, with the exception of magmatic crystallization. The deformation of rocks is defined as the change in their fabric, i.e., the changes in the shape and mutual position of the mineral grains which do not affect the quality and co-ordination of the constituents of the mineral structures. Consequently, deformation includes no chemical rearrangement and does not lie within the sphere of geochemistry.

Regional metamorphism is the most common and petrologically the most important form of metamorphism. It is not limited to the exceptional contact areas, but its effects may be discerned in rather extensive metamorphic terranes, particularly in the deep zones of old geosynclines. Regional metamorphism includes all changes in structure and composition that derive from changes in temperature, pressure, and shearing stress and from the migration of matter. Regional metamorphism may be divided into two groups of processes:

1. Changes that do not affect the bulk chemical composition of the rock: isochemical or internal metamorphism. No material migrates into the rock or from the rock.
2. Changes that affect the bulk chemical composition of the rock, involving substantial addition or removal of matter: allochemical or metasomatic metamorphism.

The metamorphism of a rock hardly ever is purely internal metamorphism. Metasomatic migration of matter characterizes all natural metasomatic phenomena, even though its rate and degree vary.

The internal metamorphism, strictly speaking, does not belong in the domain of geochemistry because it does not involve changes in the bulk chemical composition of the participating rocks. The differentiation, in this particular instance, is confined to the distribution among the rock-making minerals, and consequently its dimensions

are very much smaller than those of geochemical differentiation in the major and in the minor cycle. The manner of occurrence of an element in rocks is of geochemical interest only in so far as it may decide the manner of participation of the element in its geochemical cycle. The internal metamorphism, however, may change the solubility of the compounds of an element and consequently affect its geochemical cycle. New minerals form in internal metamorphism, and in their structures the binding forces between the ions and the atoms may differ from those existing in the original structures. Therefore, either the elements become detached from the new structures more readily than from the original ones, or they are more tightly bound in the new structures. Geochemically speaking, however, metasomatic metamorphism is more important than internal metamorphism, the reason being that metasomatic metamorphism consists of the endogenic migration of matter during the major cycle and is an essential part of that cycle.

INTERNAL METAMORPHISM

In metamorphic processes, as in all natural phenomena, the state of equilibrium and the direction of possible reactions depend on the magnitude of free energy. Under given circumstances the mineral paragenesis of a rock or the assemblage of its minerals is in a state of equilibrium, i.e., the combination of the constituting mineral structures has been arranged to have a minimum of free energy. With a change—for example, in temperature—the free energy of the system may no longer represent the minimum that the system can have at the new temperature. It follows that the rock, which retains its bulk chemical composition unchanged, rearranges and develops a new combination of structures that has less free energy than the original combination did. If the rearrangement takes place, the mineral constituents of the rock react with one another to form new minerals, and metamorphism continues until a new equilibrium has been set up.

It must be noticed that the changes in free energy which govern the equilibrium only indicate the direction in which the reactions tend to proceed. In a static state, when the changes in external factors are relatively slow and the rates of reaction sufficiently high, the equilibrium may be reached readily enough. On the other hand, always when strong movements caused by directed pressure or shearing stress are connected with metamorphism, an equilibrium is more

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difficult to reinstate. The penetrative movements that take place in a rock cause translations or internal slip in the structures of minerals, thereby preventing the reinstatement of equilibrium. They also promote the removal of ions from their co-ordination and consequently favor the formation of a dispersed phase (see below). Furthermore, strong movements indirectly oppose the reinstatement of equilibrium, inasmuch as the pressure-temperature conditions due to the movements may locally change at a rapid rate, which may sometimes be too fast to allow a corresponding adjustment of the rate of reaction.

When penetrative movements affect extensive areas, the differences in the elastic properties of rocks, among other causes, are responsible for the appearance of more or less abrupt local changes in pressure and in temperature in the form of maxima and minima. In addition, the maxima and minima change constantly during the movement of the rock masses. Moreover, the movements cause the migration of the dispersed phase from place to place and consequently produce irregular changes in the bulk chemical composition of the rock. Therefore, the metamorphic field is rather inhomogeneous. This result explains the presence, in rocks metamorphosed under the action of strong movements, of minerals and mineral assemblages that do not represent an energetic equilibrium and that are unstable in static conditions. The penetratively deformed metamorphic rocks often contain minerals that evidently would not form in other conditions in rocks of a similar composition. The minerals typical of penetratively deformed rocks include, among others, glaucophane, a Mg-rich Na amphibole, and the mica paragonite, $\text{NaAl}_2[(\text{OH}, \text{F})_2 | \text{AlSi}_3\text{O}_{10}]$.

In a metamorphic reaction the mineral structures will be gradually torn down, ion by ion. Disorder is created from order, but finally new structures, different from the old ones, will be formed. The reactions breaking down the old structures and making the new ones may take place in a liquid phase, called the intergranular film, into which the ions from the old structures are collected and from which they are released into the new structures to be formed. However, the presence of a liquid phase is not necessary because the structures may react with one another in the solid state, whereby the ions simply are rearranged to form the new structures.

The kinetic energy of participating ions may be used to explain the mechanism of metamorphic reactions. At a given temperature the ions of a structure are in a state of thermal vibration, and each of the

ions possesses a given amount of kinetic energy. The kinetic energy of an ion depends on temperature, but even the ions of the same element in a structure have different amounts of kinetic energy due to variations in their amplitude of vibration and to the corresponding variations in the number of collisions between the ions. Therefore, only the statistical average of the kinetic energy of the ions of an element remains stable at a given temperature. For some ions of the structure the kinetic energy momentarily may exceed the migration energy (see under "Crystal Chemical Discussion of the Course of Crystallization," p. 169). When this happens, the ion is liberated from its co-ordination and may migrate into a new one. It follows that some ions are always present that are not strictly and rigidly bound to a certain structure but form a separate phase, called the dispersed phase. In a state of chemical equilibrium the number of ions migrating from the structures into the dispersed phase is equal to the number of ions moving in the opposite direction. The amount of the dispersed phase or the number of free ions depends on temperature. At elevated temperatures the kinetic energy of the ions is high, and consequently the number of free ions increases, whereas at low temperatures it is less probable that an ion, by incidental collisions with other ions, may reach the threshold value of the migration energy. Therefore, at low temperatures the quantity of the dispersed phase in a rock is small. Along with temperature, pressure affects the quantity of the dispersed phase. Provided that temperature and pressure remain constant, the crystalline phase is in equilibrium with the dispersed phase; but, with changes in the environmental factors, the quantity of the dispersed phase will fluctuate.

The concept of the dispersed phase may be used to illustrate the chemical activity of an element or of an ordered structure (a mineral) in metamorphic reactions. It is evident that an ion rigidly bound within a structure is chemically inert. Such an ion may react, i.e., become attached to another structure only when released into the dispersed phase. This phase may be compared with a highly compressed gas, and consequently the chemical activity of an ion is comparable to its partial vapor tension in the dispersed phase. The chemical activity of the structure as a whole is equal to the sum of the partial tensions of the dispersed ions, which are in equilibrium with the structure under the circumstances in question. Owing to the thermal vibration and to the mutual collisions of its ions, every ordered structure always exerts a certain pressure (pressure of dispersion or vapor

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tension) which is the force expelling the ions from the structure into the dispersed phase. In a state of equilibrium the pressure of dispersion is equal to the sum of the partial tensions of the ions present in the dispersed phase. The pressure of dispersion of the structure has low values at low temperatures and at low external pressures, and consequently the chemical activity of the structure and the rate of possible reactions is then low. On the other hand, under the circumstances of natural metamorphic reactions the pressure of dispersion is considerably higher and the rate of reaction rapid enough to cause metamorphism.

METASOMATIC METAMORPHISM

The Earth's crust as a whole is often treated as a huge physico-chemical system, but such a viewpoint seems to be likely to lead to hypotheses and generalizations that are not always applicable to real geological units. It must be emphasized that a completely closed system is unthinkable in Nature, and therefore any part of the Earth's crust should always be considered with adequate reference to its surroundings, viz., the adjoining rocks or the other geospheres. In the statistical treatment of chemical phenomena in the upper lithosphere the possible effects of geological processes should also always be considered.

The presence of a dispersed phase is the condition of all chemical reactions that take place in rocks. The dispersed phase may be a liquid or a gas or it may consist of ions temporarily detached from their original places in mineral structures. Even in reactions between solid substances the ions are removed from their original structural positions and move into the new structure in a disordered state, that is, through a dispersed phase.

The reactions in the solid state, studied by a number of silicate chemists and physicochemists, above all by J. Arvid Hedvall in Sweden and by Gustav Tammann, Wilhelm Jander, and Wilhelm Jost in Germany, have found wide application in the explanation of metamorphic processes. Eskola (1934) discussed some geological implications of solid diffusion, maintaining the view that, in crystalline schists which are metamorphosed in the upper zones of mountain chains, diffusion and reactions in the solid state probably have been considerable. Since then a number of highly controversial papers on the role of diffusion in metasomatic metamorphism has been published, representing various approaches to the problem. Thus far, no uniformity of opinion has been reached, and it is frequently emphasized

that the conditions required to maintain diffusion are seldom, if ever, met in the Earth's crust. Therefore, many of the discussions would seem to be purely hypothetical. Furthermore, it is hard to find indubitable evidence of reactions in the solid state in rocks.

In any case, all chemical reactions in solid rocks are connected with the migration of ions, i.e., by their diffusion. The physical and chemical properties of mineral structures determine the nature of the diffusion processes in rocks. In the simple change of a structure into another, e.g., in the transformation of andalusite, $\text{Al}_2[\text{O}|\text{SiO}_4]$, into sillimanite, $\text{Al}[\text{AlSiO}_5]$, the extent of diffusion, or the length of its path, is of the same order of magnitude as the distances of ions in the structure. If the structures that react with one another are found in the same rock, the diffusion distance may vary from some millimeters to several centimeters. The occurrence of diffusion under these circumstances is understood well enough. On the other hand, the migration of elements, within a geological formation, from one rock into another or from one geological formation into another may cover distances that are measured in kilometers and tens of kilometers.

Buerger (1948) emphasized the decisive role of temperature in diffusion, stating that, whenever temperature is high enough to cause spontaneous growth of crystals, it is already maintaining a very high level of diffusion, because of its disordering tendency, and therefore the smaller atoms and ions of a structure may be expected to migrate rather freely through the remainder. Consequently, wholesale diffusion must be important for the transfer of matter in metamorphism.

Ramberg (1944, 1945*a*, *b*, 1946*a*) discussed diffusion on the basis of the forces which govern the movement of ions in rocks. In his opinion, diffusion is comparable to osmotic phenomena. The rocks assume the role of semipermeable membranes, through which the ions diffuse in solutions. Depending on the composition of the rock and on the external conditions, different atoms and ions penetrate through a rock at different rates. The difference of pressure on both sides of the semipermeable membrane determines the direction and rate of diffusion. In a similar manner the partial vapor tension of an atom or of an ion in the dispersed phase will determine the chemical activity of the atom or ion in question during the migration. The greater the chemical activity of an atom or ion, i.e., the higher its partial vapor tension in the dispersed phase, the greater is the possibility of its migration in the upper lithosphere. The force causing the diffusion of an ion from a place (*A*) to another (*B*) consequently depends on the

difference between the partial vapor tension of the ion in the dispersed phase at *A* and at *B*, i.e., on the vapor tension gradient between *A* and *B*. The ions contained in the dispersed phase start to migrate from *A*, where the chemical activity is high, and, in order to re-establish equilibrium between the solid phase and the dispersed phase at *A*, new ions are transferred from the structures of minerals into the dispersed phase. At *B*, where, owing to external factors, chemical activity is low, the ions of the dispersed phase will enter the solid phase, and equilibrium is reinstated by the migration of new ions to *B*. Consequently, three stages may be distinguished in the transfer of matter, viz., dispersion of atoms and ions at places of high chemical activity, migration or diffusion of the dispersed particles to places with lower chemical activity, and transfer of the particles from the dispersed phase to the solid structures (consolidation).

The difference between the chemical activity of a given structure at *A* and at *B* depends on the difference in temperature, pressure, chemical composition, concentration, and stability of phases between *A* and *B* and on the grain size of the solid phases at *A* and *B*. All this indicates that certain gradients between *A* and *B* are the condition of migration. According to Ramberg, the explanation of migration is not necessarily the mechanical transportation of a separate liquid or gaseous phase. Purely chemical forces, that is, differences of chemical activity in a metamorphic field, are the primary cause of migration.

In Ramberg's discussion the approach lies in the application of the vapor tension of compounds and of their constituents, but Bugge (1945) thought that a better approach is the application of chemical potentials in all diffusion processes. Differences in external pressure induce differences in chemical potential, and this causes the migration from places of high pressure to those of low pressure. Bugge distinguished between three ways of migration, viz., migration through solid, through liquid, and through gaseous phases.

The ionic migration through a mineral structure in the solid state may take place in the following ways: through open spaces and channels in the structure; by means of isomorphic substitution; or by means of vacant positions in the structures, into which the neighboring ions may jump; and along the boundaries of the crystals. It is evident that ionic migration through solid substances is greatly facilitated by the presence of disorder and defects in the structures. If a fluid intergranular phase exists, the transport along the intergranular film is too slow to prevent the diffusion through the structure. The

anions O^{2-} , OH^- , Cl^- , and F^- have big radii and probably will diffuse along the crystal boundaries, whereas the cations are smaller and may diffuse both through the structures and along their boundaries at approximately the same velocity. If no open channels exist in the rock, the migration must take place through the minerals or through the interstices between them. If the interstices are large, they serve as channels for most of the migration, but toward deeper layers in the crust the size of the pores will gradually decrease, and ionic diffusion through the mineral structures probably will begin to dominate. The rocks in the upper lithosphere, at the levels of metasomatic metamorphism, are soaked in a dispersed system of particles which moves through the interstices of the minerals and through the minerals themselves and tends to alter metasomatically every part of the rocks.

Increase in pressure produces a decrease in intergranular dimensions and consequently decreases the rate of intergranular diffusion. Increase in pressure also tends to produce more closely packed structures, and therefore the free space between the atoms and ions in structures decreases, and the rate of internal diffusion also decreases. The alkali metals are highly compressible, and consequently they become mobilized by high pressure. The greater compressibility of potassium, compared with that of sodium, may account for the preferential increase in the rate of diffusion of potassium ions with pressure. Bugge also thinks that the rate of diffusion through solid structures will increase with depth in the lithosphere because great differences in chemical potential and in chemical activity are encountered in the deep zones.

The rate of ionic diffusion depends on the size of the ion. Backlund (1936) found that the rate of diffusion of potassium, sodium, aluminum, and silicon in contact zones between granite and limestone decreases with increasing ionic radius. Bugge (1945) and Lapadula-Hargues (1945; see under "Granitization," p. 260) arrived at a similar conclusion, whereas in Ramberg's opinion (1946a) the mobility of Mg and Ca is usually low, but K, Na, Si, Fe, Mn, Li, and Be diffuse at high speed through ordinary rocks.

Rosenqvist (1947) pointed out that the application of the principles of Ramberg and Bugge to geological phenomena does not always seem to be consistent with the conditions actually existing in the upper lithosphere. In Rosenqvist's opinion, the discussions presented by Ramberg and Bugge are of only theoretical interest, except

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for reactions that take place in the solid state, in which case a dispersed phase is not present. According to Rosenqvist, a dispersed phase probably is always present, as an extremely thin film in the intergranular fissures found in all rocks. The adsorption phenomena taking place in the intergranular film are of high importance for the metasomatic processes. The nature of the solvent forming the dispersed phase also plays an important part in recrystallization and transportation. Actually, diffusion may operate both from high pressure to low pressure and vice versa.

Verhoogen (1948) emphasized the importance of surface phenomena as a controlling factor in metasomatic metamorphism. The effect of a solution impregnating a rock, according to Verhoogen, not only depends on temperature, pressure, permeability, and other factors usually considered in this connection but also on the magnitude of surface tension of the solution against the various minerals, the shape and size of the mineral grains and of the cavities and pores between the grains, and on the partial molar volume of the various constituents of the solution. Therefore, in a multicomponent system consisting of rocks and impregnating solutions, the precipitation and solution processes are extremely complicated. Even though the presence of a solvent is not necessary and material may be transported by diffusion, the solvent will accelerate the diffusion, which is a rather slow process at ordinary temperatures. This type of diffusion is independent of all external factors, such as temperature, pressure, and shearing stress, and depends essentially on the magnitude of intermolecular forces and on the type and closeness of packing in the structures.

In pneumatolytic and hydrothermal metasomatism the elements introduced are often those in which the silicate melt that produced the solutions and gases is itself deficient; thus skarns rich in silicate minerals of iron and magnesium are formed at contact zones between granite (granodiorite) and limestone. This is the rule of polarity (Lodochnikov, 1936).

The metasomatic changes often pronouncedly affect the chemical composition of rocks. According to the elements introduced, the metasomatic processes may be divided into the following five groups (Eskola, 1939b):

1. Introduction of alkali metals (alkali metamorphism)
2. Introduction of calcium (lime metasomatism)
3. Introduction of iron, magnesium, and silicon (iron-magnesia-silicate metasomatism)

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4. Introduction of boron, lithium, fluorine, chlorine, sulfur, silicon, and tin (boron metasomatism, etc.)
5. Introduction of carbon dioxide (carbon dioxide metasomatism)

Quantitatively, the metasomatic processes still are little investigated. Sometimes the amounts of elements introduced are enormous. Emmons and Calkins (1913) presented evidence that the quantity of scapolite formed metasomatically in the sediments of the Philipsburg area in Montana in the United States corresponds to the introduction

TABLE 5.58

MINIMUM ESTIMATES OF METASOMATICALLY INTRODUCED AND REMOVED COMPOUNDS IN LIMESTONES AROUND THE OPHIR HILL CONSOLIDATED MINE IN UTAH

Introduced Compound	Quantity in Tons
SiO ₂	900,000
Al ₂ O ₃	270,000
Na ₂ O.....	10,000
K ₂ O.....	160,000
H ₂ O+.....	22,000
TiO ₂	11,000
P ₂ O ₅	9,000
S.....	12,000
FeS ₂	380,000
PbS.....	200,000
ZnS.....	200,000
Cu.....	5,000
F.....	3,000
Total.....	2,182,000
Removed Compound	Quantity in Tons
MgO.....	64,000
CaO.....	1,026,000
CO ₂	964,000
Total.....	2,054,000

of an amount of chlorine that must be measured in cubic kilometers at ordinary temperature and pressure. Gilluly (1932) found that a very remarkable transfer of material occurred during the metasomatic production of sulfide-ore bodies in limestones in the Stockton and Fairfield quadrangles in Utah in the United States. For an area of about 280,000 m², in which the thickness of the limestone beds is about 18 m, Gilluly gives the estimates of the minimum quantities of materials introduced and removed shown in Table 5.58. The quantities of the minor elements, such as titanium, phosphorus, sulfur, and fluorine, are especially remarkable, considering the fact emphasized by Gilluly that his estimates actually may represent less than a quarter of the total brought into the area investigated.

ENDOGENIC MIGRATION OF MATTER IN
THE LITHOSPHERE

No thermodynamic equilibrium has been fully established in the Sial crust in places where chemical activity gradients exist. It may be proved by thermodynamic reasoning that an equilibrium would be established in the lithosphere if the rocks were arranged, according to their properties, into concentric and coherent shells. However, at least in the salic continental masses, no concentric arrangement has been attained, and the geochemical differentiation phenomena in the upper lithosphere, along with the radial and tangential movements of the rock masses, suffice to prevent the achievement of thermodynamic equilibrium. Geochemical differentiation, mountain-building processes, and isostatic movements, together with other causes, set up thermodynamic disequilibria in the Sial crust, but they also start the endogenic migration of matter, which tends to reinstate the equilibrium. At the deep levels of the upper lithosphere that are no longer affected by the mountain-building movements, approximate equilibrium has probably been reached because, at the elevated temperatures and high pressures prevailing in the depths, the velocity of diffusion is higher than at the upper levels. Near the surface the rate of diffusion and the chemical activity are low enough completely to suppress the migmatitization processes which constitute the most important form of migration of matter in the upper lithosphere. The boundary of the zone of migmatitization is called the migmatite front. Its depth in the Earth's crust varies in the different geological units.

The endogenic migration of matter in the lithosphere is geochemically characterized by its selectivity, which means that under given circumstances certain elements are able to migrate more readily than others. The pressure of dispersion depends, among other things, on the structure and composition of the minerals, and the mobility of the atoms and ions constituting the minerals depends on the atomic weight and density of the dispersed structures or particles. With increasing pressure the heavy atoms often may pass into the dispersed phase more readily than the light ones, and structures of low density disperse more readily than those of high density. As a matter of fact, the elements with high atomic number are relatively readily mobilized and become enriched in granites and in low-temperature assemblages in general, i.e., in rocks and minerals that may be assumed to

have formed through rather significant circulation and migration of matter.

The effect of the gravitational field on chemical equilibria in the Earth's crust was also thermodynamically analyzed by Ramberg (1946*b*, 1948). He concluded that some elements with low fictive density (atomic weight divided by fictive molar volume) will chemically squeeze out of the deeper levels of the crust. Consequently, water, silica, carbon dioxide, and oxygen are squeezed out from minerals at great depth and diffuse upward and may participate in metasomatic reactions. In addition, ions of large dimensions and of low fictive density, such as K^+ , Na^+ , and F^- , will squeeze out of the minerals or magmas and migrate upward, being, in part, responsible for migmatitization and granitization. Higher oxides of iron are similarly unstable and split into oxygen and iron. In general, elements with high fictive density tend to become gradually concentrated at the lower levels in the crust, and the elements with low fictive density migrate upward unless the interatomic binding forces counteract gravity. Gravity also affects the distribution of oxygen at different levels in the crust. Therefore, the redox potential varies, partly because of upward diffusion of oxygen and partly because of downward movement of the elements with high fictive density.

Barth (1948) applied Ramberg's analysis to a theoretical study dealing with the cycle of oxygen in the upper lithosphere. Because the bulk of the lithosphere consists of oxygen and because the big O^{2-} ions probably are rather stationary, cations will migrate in the glassy oxygen solvent and produce a vertical oxygen gradient. When highly oxidized sediments and surface rocks are pushed down in orogenic movements, oxygen is released and gradually returns to the surface, partly in rock-making minerals, partly as water and carbon dioxide. Atomic oxygen may also form from dissociating oxide minerals at high temperatures and pressures.

It is evident that migration phenomena are highly important in molding the chemical composition of the uppermost lithosphere. Ranskama (1946) found evidence of a global migration of elements in the Earth's crust that causes the separation of many elements into two groups, viz., the granitophile and the granitophobe elements. The granitophile elements are those known to be especially enriched in granitic rocks, either of igneous or of quasi-igneous origin. They endeavor to concentrate in the outermost parts of the crust, whereas

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the granitophile elements are pushed down toward the basaltic substratum (see chap. 10).

GRANITIZATION

When a truly magmatic phase (silicate melt) is incorporated into the metasomatic rearrangement of a rock, the product is a migmatite or a mixed rock. Probably the migmatitizing liquid usually is a granitic residual melt rather than an aqueous hydrothermal solution. Other migmatites may be the result of differential anatexis of originally solid rocks. The third possibility of migmatitization is a molecular diffusion by means of a liquid phase or in the solid state. All these processes tend to give a granitic composition and appearance to rocks of highly varying origin and chemical composition. It is probable that all these factors are effective in the production of huge masses of granite of a typically igneous appearance.

The granitization or the formation of granites in migration, anatexis, and palingenesis is one of the key problems of metamorphic petrology. Evidence of granitization is found in every orogeny, and probably granitization processes characterize certain stages of all orogenic cycles.

Actually, all rocks in the uppermost crust are nothing but islands in a solid granitic ocean. The gravitative stratification of the uppermost lithosphere, according to common belief, has resulted in the formation of an upper granitic crust lying upon a basic layer, gabbroic or basaltic in composition. Eskola (1932*b*) expressed the view that the gravitative stratification is probably due to two processes, viz., crystallization differentiation, combined with the squeezing-out of the residual melt, and partial re-fusion of already solidified rocks, with subsequent squeezing-out of the molten part. The two processes produce a fluid, called the granitic ichor, which slowly rises into the superposed rocks and gives them a granitic or granite-like composition. The chief constituents of the ichor are silicon, aluminum, sodium, and potassium, which are concentrated in the last differentiates during the magmatic crystallization and which also are the first elements to become mobilized in anatexis. Oxygen and hydroxyl ions also migrate in the ichor, along with the four cations. According to Bugge (1945), radioactive elements are often mobilized in remelting and migrate in the ichor. The distance that the ichor moves may range from a few millimeters to several kilometers. There is probably enough time to account for a long-distance migration of the ichor, but

a long-distance diffusion through solid minerals, in Bugge's opinion, must still be considered hypothetical.

However, it does not seem necessary for the ichor, which may be called a dispersed system of particles, always to be a liquid. Ionic diffusion may also be applied to account for granitization, and it is probable that both pore solutions and diffusion in the solid state participate in the process. Granitization evidently is one of the most important manifestations of the migration of matter in the upper lithosphere.

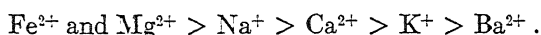
If the principles of migration are applied to granitization, the mechanism of the process may be explained in the following way: The binding forces in the quartz and feldspar structures are rather weak. Consequently, the ions will disperse readily from these structures and migrate to places where chemical activity is low and where consolidation will take place. According to Ramberg (1945c, 1946a), the chemical activity, because of pressure differences, is lower below the geosynclines than below the continents. Therefore, dispersion of matter will take place under the continents, the direction of migration is toward the geosynclines, and consolidation takes place below the geosynclinal sediments. Here the chemical activity is low enough to cause the formation of even quartz and feldspar from the migrating atoms and ions. As long as the basic layer of the lithosphere is incompletely differentiated, it is responsible for the granitization, either by the slow upwelling of granitic magma or by diffusion.

Migmatitization and granitization are nothing but contact metasomatism of regional dimensions. Similar mechanisms may be held responsible for the formation of other quasi-igneous rocks, i.e., those produced by granodioritization, gabbroization, and other comparable processes.

The discussion of granitization presented above shows that igneous-looking rocks are believed to exist which have not crystallized from a melt but are produced by reactions in the solid state, viz., diffusion and migration of huge dimensions in the uppermost lithosphere. Therefore, it is probable that all gradations exist from juvenile granites of a truly magmatic origin to metasomatic granites and to paligenetic granites formed by differential or total anatexis under the action of granitizing liquids and vapors or entirely by the migration of atoms and ions resulting from a chemical or thermodynamic instability in the Earth's crust.

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The statistical studies of Lapadu-Hargues (1945) showed that in rocks submitted to regional metamorphism of varying intensity the concentration of certain elements varies and depends on the differences in the mobility of the elements in metamorphic processes. The order of decreasing mobility, according to Lapadu-Hargues, is



The mobility is evidently a function of the ionic radius. Ferrous iron and magnesium, which have the smallest ionic radii, are the most mobile elements among those investigated. During granitization they tend to become concentrated in the least altered sediments, farthest from the totally granitized ones. This agrees with field observations, which show that iron and manganese are mobilized in migmatitization and granitization and become concentrated in the so-called basic front, which is the precursor of the fronts of migmatitization and granitization. Reynolds (1946) has shown that phosphorus, manganese, and titanium are also released in granitization and that these elements, along with iron, magnesium, some potassium, and sometimes sodium, are all fixed in the basic zone beyond the zone of granitization. There is field evidence which shows that a basic zone, in one form or another, actually is connected with all granites, independent of their origin. The iron-magnesium front is particularly well developed in rocks that initially were relatively basic, and such rocks often remain as basic inclusions in the granites. Because the content of femic constituents in the basic zone is high, the zone is relatively impoverished in silica (zone of desilicification). According to Reynolds, the materials of the basic front are constantly being driven out from zones in which the granitization has been completed into the neighboring ones, in which they act as precursors of the front of granitization. Potassium, however, is also strongly concentrated in the rocks representing the final stage of granitization.

The results presented above show that there is a mutual dependence between granitization and basification. According to Reynolds (1946, 1947), in every instance for which adequate chemical data are available the emplacement of granitic bodies has been accompanied by the introduction of calcium, iron, and magnesium into both aureoles and inclusions, and the basified rocks have been granitized only subsequently.

It is evident that magmatic differentiation is not the only process capable of producing great quantities of igneous-looking deep-seated

rocks. The silicic rocks, in particular, often seem to be the result of metasomatic processes in the upper lithosphere, and therefore the classical theory of differentiation by crystallization evidently loses some of its significance. However, the theory of magmatic differentiation explains the behavior of the elements during the crystallization of rock melts and consequently is important as the basis of the estimation of the mobility of the elements in metasomatic metamorphism.

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OCCURRENCE AND AMOUNT OF WATER ON THE EARTH

THE lithosphere is partly covered by a water blanket called the hydrosphere. Actually, the greater part, or 70.8 per cent, of the Earth's surface is covered by water. The oceans form by far the greatest and most important part of the hydrosphere. The total area of all oceans, including the adjacent seas, is, according to Kossinna (1921), $361.059 \cdot 10^6$ km², their total volume being $1,370.323 \cdot 10^6$ km³. The area of all dry land is $148.892 \cdot 10^6$ km². The mean depth of the oceans is 3,795 m. Assuming the density of the ocean water to be $1.026 \text{ g} \cdot \text{cm}^{-3}$, one finds the total mass of the ocean to be $14,060 \cdot 10^{20}$ g, or 14,060 Gg.¹

Salt water also occurs on some isolated areas on all continents. This water never reaches the sea but gathers in depressions forming alkaline or salt lakes.

Fresh water occurs in the soil as ground water and in the pores of rocks as hygroscopic water. It flows to the surface of the Earth as spring water, fills the ponds and lake basins, and flows in rivers and streams as surface water. The permanent fields of snow, the glaciers, inland ice, and permanent ice at high altitudes consist of frozen water. Ground water mixed with juvenile water enters the volcanic emanations and hot springs. The cavities of rocks and their minerals contain salt solutions which may be of primary magmatic origin, whereas other solutions consist of water of meteoric origin trapped in the rocks. According to W. Halbfass (in Meinardus, 1928), the total volume of water in lakes and that of the river and ground water are approximately 250,000 km³, whereas the volume of ice is many times higher. It is calculated that 10.1 per cent of the total land area is now covered by ice and snow. The total area of the existing glacier ice is 15,100,035 km², and its volume is 9,528,249 km³ (S. Thorarins-

1. One geogram, or Gg, is 10^{20} g (Conway, 1942).

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son; according to Flint, 1947). If all this ice melted to water, the corresponding rise of sea level would be around 24 m, minus an allowance due to the isostatic adjustment of 5–10 m. The volume of water vapor in the atmosphere corresponds to about 13.000 km³ water, its mass is $13 \cdot 10^{18}$ g, or 0.13 Gg.

Goldschmidt (1933a) estimated that for every square centimeter of the Earth's surface there are 273 liters of water, made up as follows:

	liters		kilograms
Sea water.....	268.45	or	278 11
Fresh water	0.1		0 1
Continental ice	4.5		4 5
Water vapor.....	0.003		0.003

It might be noted that the amount of the different kinds of water changes continually. Juvenile water is constantly added to the surface waters. The amount of water in glaciers and continental ice is bound to change according to the variations in the climate, as is the case during the present glacier shrinkage.

According to the above figures, the fresh water, ice, and atmospheric water form only about 2 per cent of the total amount of all water present in the hydrosphere. This figure has but little effect on the calculation of the average composition of the hydrosphere, and it is consequently appropriate to state that the composition of the hydrosphere is that of ocean water; the other parts of the hydrosphere may be omitted in this connection.

Water possesses some unique physical properties which are not without importance as far as its geochemical behavior is concerned. Studies of related compounds show that the freezing point of pure water should lie at -150° C. and its boiling point at -100° C. The values actually observed, viz., 0° C. and 100° C., respectively, are explained by the polymerization of water. Another fact of importance in the geochemistry of water is that, among all liquids, it is especially suitable to the various needs of organisms.

All natural waters in their various states are actually rocks formed by the mineral water, H₂O. The natural waters are, however, never pure because they contain various gaseous or dissolved and particulate impurities. As pointed out by Vernadsky (1930), the waters form a very cohering group because water changes easily from one physical state into another, depending on the thermodynamic circumstances prevailing in Nature. Thus gaseous, liquid, and solid water are always found to coexist.

WATER IN THE CAVITIES OF MINERALS AND ROCKS

Rocks are known to contain salt solutions in their cavities or as microscopic or larger inclusions in their minerals. The discussion in chapter 5 has shown that water is, quantitatively, the most important constituent of volcanic emanations. During the crystallization of magmas, water, along with other volatile constituents, is concentrated toward the later stages of the process.

H. C. Sorby, in 1858, made the first thorough study of the microscopic cavities of rock minerals and proved that the liquid found therein consisted of water with dissolved chlorides and sulfates of alkali metals and calcium. Analyses of liquid in inclusions in quartz of Alpine mineral vugs were made by Königsberger and Müller (1906*a*, *b*), who give the average composition for these liquid inclusions, shown in Table 6.1.

TABLE 6.1
AVERAGE COMPOSITION OF LIQUID FROM
INCLUSIONS IN QUARTZ

Compound	Per Cent by Weight
H ₂ O.....	85
CO ₂	5
Na.....	2.5
K, Li.....	1.5
Ca.....	0.3
CO ₃	3.5
Cl.....	1.5
SO ₄	0.7
Total.....	100.0

Faber (1941) published a number of analyses of salt solutions, chiefly from the cavities of granites. His results showed that the quantity of salt solution in the cavities amounted to 0.13–0.40 per cent by weight of the rock. The liquid contained between 6.6 and 22 per cent of dissolved salts. The total salts amounted to 0.133–0.737 parts per thousand by weight of the rock. Some of Faber's analyses showing the composition of the salt solutions are given in Table 6.2. Chlorides predominate in the salt solutions from granites. Similarly, the chlorides are the chief salts in the cavities of pegmatite quartz, whereas sulfates predominate in pegmatite orthoclase.

Large reservoirs of water are sometimes met in mines, impounded in the rocks. Bruce (1941) published an analysis of a mine water which is reproduced in Table 6.3, together with the analysis of a mine water presented by Clarke (1924). These waters are very pure

TABLE 6.2
COMPOSITION OF SALT SOLUTIONS FOUND IN
THE CAVITIES OF ROCKS

Rock	ASSUMED SALTS, PARTS PER THOUSAND					TOTAL SALTS, PARTS PER THOUSAND BY WEIGHT OF ROCK	WATER IN CAVITIES, PER CENT BY WEIGHT OF ROCK	SALTS, PER CENT BY WEIGHT OF LIQUID
	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	CaSO ₄			
Rønne granite, pre-Cambrian, Bornholm, Denmark...	0.120		0.185	0.102		0.407	0.20	17
Svaneke granite, pre-Cambrian, Bornholm, Denmark...	0.315	0.240		0.097	0.085	0.737	0.38	16
Granite, Permo-Carboniferous, Princetown, Devon, England.....	0.371		0.034		0.037	0.442	0.40	10
Basalt, Trangisvaag, Suderø, Faeroe Islands	0.108		0.138			0.245	0.23	10

TABLE 6.3
COMPOSITION OF MINE WATERS

Constituent	Water, Sturgeon River Gold Mine, Canada	Water, Quincy Mine, Hancock, Michigan, U.S.A.
	Per Cent by Weight	
Cl.	63.32	63.55
SO ₄	0.02	0.01
CO ₃	n.d.	0.01
PO ₄	n.d.	0
Na.	7.24	5.63
K	0.002	0
Ca	29.40	30.78
Mg	trace	0.01
Al	n.d.	0
Fe (ferrous)	n.d.	0
Mn, Co	n.d.	0
SiO ₂	n.d.	0.01
Au	0	n.d.
Total.	99.982	100.00
Salinity (p.p.m.)	154,950	212,300

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chloride waters, containing calcium and sodium as the only important cations.

Liquid carbon dioxide is a common constituent of inclusions in quartz. Hydrocarbons or petroleum-like substances and hydrogen sulfide are also reported to occur as liquid inclusions in minerals. Newhouse (1932) found NaCl and CaCl₂ in galena and sphalerite cavity solutions in minerals from localities widely differing in their geological relations. The presence of these chlorides suggests that the sulfides were carried in solution chiefly with sodium chloride.

During weathering the cavity solutions are liberated, except from the most resistant minerals, and are subsequently incorporated into the weathering solutions.

GROUND WATER

Ground water is an aqueous solution of chiefly bicarbonates, sulfates, and chlorides of the alkaline-earth and alkali metals. The amount of the dissolved solids depends on several factors, e.g., the origin of the water, the composition of the adjacent rocks and soils, and the length of time that the water has been in contact with the surroundings.

The meteoric waters, i.e., those of atmospheric origin, contain carbon dioxide and small amounts of dissolved substances derived from the atmosphere. Upon entering the soil and rocks, they first incorporate soluble constituents, both inorganic and organic, from the soil. Additional carbon dioxide is also derived from humus and other organic substances, partly by the action of dissolved oxygen in the water. The ground water charged with carbon dioxide is a powerful weathering agent, able to break up nearly all minerals and to form new compounds consisting of carbonates, bicarbonates, and sulfates of sodium, potassium, calcium, and magnesium, soluble alkali silicates, and free silica in true or colloidal solution. On the other hand, aluminum, iron, and silica remain, for the most part, in the insoluble residue. The rate of decomposition depends on the chemical composition and physical properties of the rock minerals and on the temperature. Sodium and potassium are leached out rapidly, whereas the rate in the case of calcium and magnesium is lower.

Another group of ground waters, called connate waters, contains substances which were present in solution at the time that the sediment beds soaked with such waters were deposited.

A number of physical and chemical causes are active in changing the composition of the ground waters percolating through soil and

rock. The concentration may change through evaporation. Base exchange, adsorption, oxidation of sulfides, and reduction of sulfates cause changes in their chemical composition, as well as the mixing with other waters, e.g., connate waters. Base exchange usually results in the softening of the ground water when brought into contact with materials releasing sodium in exchange for calcium and magnesium. On the other hand, concentrated NaCl solutions may substitute sodium in minerals in exchange for calcium and magnesium previously removed from hard water. The bases and acids formed by the hydrolysis of salts of weak acids and strong bases, or vice versa, are readily adsorbed without substitution. Consequently, the bases formed from alkali and alkaline-earth carbonates, silicates, and phosphates are adsorbed to form silicates, whereby the concentration of the acid radicle may increase considerably. On the other hand, the silicate and phosphate anions of the alkali silicates and phosphates are partly removed by soils, chiefly by reactions with $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, which lead to the formation of insoluble compounds. The reduction of sulfate in ground water is attributed to the presence of organic matter and sulfate-reducing bacteria.

The composition of ground water is very variable, ranging from that of nearly pure rain water (see chap. 7) to that found in mineral wells and springs.

SPRING WATER

The composition and salinity of spring water depend on local conditions. Sulfates and carbonates are the most important constituents of spring water, whereas chloride is usually less important. The silica content may sometimes be rather high. Calcium is, quantitatively, the most important cation, and consequently the spring and well waters are hard. Two analyses of spring water given by Clarke (1924) are reproduced in Table 6.4. Usually the amount of carbonate exceeds that of sulfate, but, if much sulfides or sulfates are present in the percolated beds, the content of sulfate may be very high.

Pfeilsticker (1936) investigated the Ba:Sr ratio in spring water percolating through formations of different geological age in the Stuttgart area in Germany. Notwithstanding the great similarity in the hardness of the waters, notable variations were found in the Ba:Sr ratio:

Springs in	Average Ba:Sr ratio
<i>Lias a</i>	0.16
<i>Keuper</i>	1.2
<i>Muschelkalk</i>	1.0
<i>Buntsandstein</i>	5.6

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Thus the Ba:Sr ratio in many cases offers a clue for distinguishing between the various formations.

WATER IN LAKES AND RIVERS

On its way to lakes and rivers the flowing spring water changes rapidly in composition, owing to mixture with precipitation, surface waters, and other ground waters. Pollution by sewage and industrial waste waters may also cause very considerable changes in the chemi-

TABLE 6.4
ANALYSES OF TWO SPRING WATERS FROM
THE UNITED STATES

CONSTITUENT	CARBONATE-DOMINANT WATER. SPRING NEAR MAGNET COVE, ARKANSAS	SULFATE-DOMINANT WATER. SPRING NEAR MOUNT MICA, PARIS, MAINE
	Per Cent	
CO ₃	53 59	6 22
SO ₄	3 40	60 97
Cl	1 35	trace
Ca	30 95	22 37
Mg	3 45	2 62
Na	1 08	4 32
K	0 63	0 21
SiO ₂	5 55	2 80
Fe ₂ O ₃	n.d.	0 49
Total	100 00	100 00
Salinity (p.p.m.)	224	606

cal composition of the waters. Some dissolved substances may be precipitated and others brought into solution from the beds of the streams. Changes in composition are particularly met in the water of small rivers, whereas the composition of water in the great rivers is more constant.

LAKE WATER

Analyses of water from some Alpine lakes, originally published by F. E. Bourcart, are given in Table 6.5 in the form recalculated by Clarke (1924). The water of Lac de Champex represents water derived from igneous and metamorphic rocks. The Lac Noir occurs in metamorphosed arenaceous and argillaceous sediments (*Flysch*), whereas the water of Lac Taney is typical of those derived from cal-

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careous rocks. In all these waters calcium is the predominant cation, and carbonate is found in two of the waters in excess of sulfate and chloride. Sodium, potassium, and silica are high in waters which emerge from areas of igneous and metamorphic rocks, with the exception of limestones.

RIVER WATER

Water is the most important and efficient of all solvents. The precipitation on land contains cyclic salts, dissolved gases, and nitrogen

TABLE 6.5
ANALYSES OF WATER FROM ALPINE
LAKES IN SWITZERLAND

CONSTITUENT	LAC DE CHAM- PEX, CANTON VALAIS	LAC NOIR, CANTON FRIBOURG	LAC TANET, CANTON VALAIS
	Per Cent		
CO ₃	29.96	26.94	53.21
SO ₄	11.93	38.85	5.29
Cl.....	9.96	0.57	0.87
Ca.....	19.15	29.65	33.74
Mg.....	1.32	2.27	1.99
Na.....	8.32	0.64	0.75
K.....	4.00	0.38	0.74
SiO ₂	13.93	0.71	2.37
Al ₂ O ₃ +Fe ₂ O ₃ *	1.43	0.49	1.04
Total.....	100.00	100.00	100.00
Salinity (p.p.m.)..	27	270.5	122

* Includes traces of Mn.

compounds (see chap. 7). Compared with sea water, rain water is remarkable for its strong leaching action on rocks because its salt concentration is low and carbon dioxide content high. The rivers carry the weathering products in their water in the form of ionic solutions or as colloidal dispersions and particulate substances. The amount of all these compounds varies according to the climate and the composition and physical properties of rocks and soils in the catchment area. Where there is abundant rainfall and much organic matter present in the soil, the ground water becomes notably charged with carbon dioxide. As a result, carbonates dominate in river water and are largely in excess over the sulfates and chlorides, and calcium is the predominating cation. On the other hand, sulfates and chlorides tend

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to prevail in waters from arid and semiarid regions, and in that case calcium often loses its role as the predominant metal ion. In tropical regions the salinity of the river waters is remarkably low because there the rivers drain thoroughly leached tropical forests and have not very much access to fresh rocks. Consequently, the amount of sulfate is relatively low, whereas iron and aluminum are usually rather abundant and silica is especially high. The great abundance of silica is evidently due to the lateritic decomposition essential to tropical and

TABLE 6.6
ANALYSES OF RIVER WATERS

CONSTITUENT	MISSISSIPPI RIVER AT NEW ORLEANS, LA., U.S.A.	PECOS RIVER, NEW MEXICO, U.S.A.	THE AMAZON AT OBIDOS, BRAZIL	THE MAHANUDDY NEAR CUTTACK, INDIA
	Per Cent			
CO ₃	34.98	1 54	24 15	27 06
SO ₄	15 37	43 73	2 26	1 08
Cl	6 21	22 56	6 94	2 04
NO ₃	1 60	n.d.	n.d.	7 44
PO ₄	n.d.	n.d.	n.d.	0.72
Ca	20 50	13 43	14 69	15 78
Mg.....	5 38	3 62	1 40	4 62
Na.....	} 8 33	14 02	4 24	5 92
K		0 77	4 76	1 64
SiO ₂	7 05	} 0 33	28 59	33 45
Al ₂ O ₃	0 45		} 12 97	n.d.
Fe ₂ O ₃	0.13			0 25
Total.....	100 00	100.00	100 00	100 00
Salinity (p.p.m.)	166	2,384	37	86

subtropical regions, which includes the removal of much of the silica as the most essential feature. The remaining laterite thus consists mostly of hydroxides of Fe³⁺ and Al³⁺.

Some analyses of river waters from temperate and tropical regions, recalculated by Clarke (1924), are presented in Table 6.6.

Carbonates are the most important constituents of the Mississippi water. The Pecos River water is a typical example of the composition of river water in arid regions. It has a high salinity and shows the predominance of the sulfates and chlorides of the alkali metals and has a low carbonate and calcium content. The Amazon and Mahanuddy waters are tropical waters containing predominantly calcium carbonate. Their total content of dissolved solids is low.

Along with dissolved inorganic substances, the surface waters contain dissolved gases, chiefly nitrogen, carbon dioxide, and oxygen. Hydrogen sulfide is also met. Nitrates, nitrites, and ammonia derive, in part, from rain water. A number of organic substances is always present in varying quantities. Clarke (1924) gives the range of the percentage of organic matter in the dissolved solids as 3.25–59.90. The highest values are found in tropical streams, which are rich in humic substances.

AVERAGE COMPOSITION OF LAKE AND RIVER WATER

Clarke (1924) has published an extensive collection of reliable chemical analyses of lake and river waters, from which the analyses given in Tables 6.5 and 6.6 are quoted. According to the calculations presented by Clarke, the average content of dissolved substances in river water is usually 100–200 p.p.m., or 0.1–0.2 g/l. and sometimes even more. The average salinity calculated by Conway (1942) from analyses given by Clarke is 146 p.p.m. This content is considerably lower than the average salinity of sea water, which is 35,000 p.p.m., or 35 g/l. The river waters can be divided into two major groups on the basis of the composition of the dissolved solids present therein, viz., carbonate and sulfate waters. Carbonate waters are the more common of the two. This fact is responsible for the predominance of the carbonate ion in the average composition of river waters of the Earth, as compared with the content of the sulfate ion present therein.

The average composition of the salts of all river and lake waters calculated by Clarke (1924) is presented in Table 6.7. Clarke (1924) has also estimated that the river drainage brings to the ocean annually $2.735 \cdot 10^9$ metric tons of dissolved substances.

Clarke's average shows that calcium preponderates among the cations present in fresh waters. This is a fact of high geochemical importance because the amount of calcium in sea water is rather small and sodium predominates therein, as is shown by the analysis of the dissolved solids from sea water, quoted from Sverdrup, Johnson, and Fleming (1942) and presented in Table 6.7. Another fact of importance is the preponderance of carbonate and sulfate ions in fresh water, as compared with the chloride ion in sea water. Calcium and a part of magnesium are precipitated in lakes and seas in the form of carbonates, which are not readily soluble. Calcium is, in addition, precipitated as sulfates, which also are sparingly soluble. The

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removal of these compounds accounts for the enrichment of chlorine in sea water. It must also be noted that numerous marine organisms extract large amounts of calcium and magnesium carbonate from sea water to build up their shells and skeletons.

Table 6.7 shows, in addition, the composition of the solids in river water, corrected with reference to the cyclic salts carried from the ocean to the atmosphere by spraying and deposited by precipitation on the continental areas. This analysis is according to Sverdrup,

TABLE 6.7
AVERAGE COMPOSITION OF DISSOLVED SOLIDS IN LAKE
AND RIVER WATERS AND IN THE SEA WATER*

CONSTITUENT	LAKE AND RIVER WATER	RIVER WATER LESS CYCLIC SALTS	SEA WATER
	Per Cent		
CO ₂	35.15	35.13	0.41†
SO ₄	12.14	11.35	7.68
Cl	5.68	0.00	55.04
NO ₃	0.90	0.90	
Ca	20.39	20.27	1.15
Mg	3.41	3.03	3.69
Na	5.79	2.63	30.62
K	2.12	2.02	1.10
Fe ₂ O ₃ , Al ₂ O ₃	2.75	2.75	
SiO ₂	11.67	11.67	
Sr, H ₂ BO ₃ , Br. . .			0.31
Total	100.00	89.75	100.00

* Partly based on material from *The Oceans*, by H. U. Sverdrup, M. W. Johnson, and R. H. Fleming. Copyright 1942 by Prentice-Hall, Inc. Used by permission.

† As HCO₃.

Johnson, and Fleming (1942), who believe that all the chloride in river water is cyclic. Three more averages for the rain-corrected composition of the solids in river water are presented, according to Conway (1942), in Table 6.8, which also contains Clarke's average, recalculated by Conway on the basis of the average salinity of 146 p.p.m. or g./ton.

Conway has also investigated the concentration of the more common ions in river water as a function of salinity. The concentration of calcium, magnesium, and carbonate rises approximately proportional to the salinity until the latter reaches a value of about 50 g./ton. Then the rise is steeper but reaches a constant value at about

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240 g/ton. In sodium, potassium, chloride, and silica there is an increase with increasing salinity up to a value of 50 g ton. From 50 to 100 the increase is smaller, and for a salinity between 100 and 200 g/ton—where there is the maximum rise in Ca, Mg, and CO₃—K and Cl remain constant and Na and SiO₂ show a slight decrease. Beyond a salinity of approximately 220 g ton, there is a rise in the concentration when that of calcium has reached a practically constant value.

TABLE 6.8
AVERAGE AND RAIN-CORRECTED COMPOSITION OF
DISSOLVED SOLIDS IN RIVER WATER

CONSTITUENT	COMPOSITION OF TOTAL RIVER WATER FOR SALINITY OF 146 p.p.m.	COMPOSITION OF RAIN-CORRECTED "IGNEOUS" WATER	COMPOSITION OF RAIN-CORRECTED TOTAL RIVER WATER	COMPOSITION OF RAIN-CORRECTED "SEDIMENTARY" WATER
	Parts per Million			
CO ₃	51.2	15.5	51.2	63.1
SO ₄	17.7	0.5	16.6	22.0
Cl	8.30	0.2	9.0	9.0
NO ₃	1.31			
PO ₄	0.34			
Ca	29.8	5.8	29.6	37.5
Mg	5.0	0.9	4.4	5.6
Na	8.4	2.8	3.8	4.1
K	3.1	1.6	2.9	3.3
Fe ₂ O ₃ , Al ₂ O ₃ . .	4.02			
SiO ₂	17.1	10.3	17.1	19.4
Other constituents		1.4	5.7	7.1
Total	146.27	39.0	131.3	162.1
Salinity (p.p.m.)	146	39	131	162

The sulfate concentration follows an intermediary course between the two foregoing groups. Conway explains these changes in the following way: Up to a salinity of 50 g ton the drainage comes from igneous and metamorphic rock areas. In the range from 50 to 200 g ton a sharp change sets in, with the beginning of drainage from sedimentary rocks, until saturation is reached at the upper limit for waters coming presumably only from areas of sedimentary rocks. The later rise in sodium, potassium, chloride, and sulfate is explained either by human contamination on a large scale or by drainage from salt beds and semiarid plains rich in salt.

Conway's calculations show, further, that almost all the chloride

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drained from igneous and metamorphic rocks and from sedimentary rocks is cyclic, being originally contained in rain water and, in the latter case, also in connate waters. The amount of chlorides delivered by volcanic emanations is found to be only a negligible part of all the chloride present in river waters. The values in Table 6.8 are calculated on the basis of the assumption that 95 per cent of the chloride in water from igneous and metamorphic rocks is cyclic and that all the chloride in the total and "sedimentary" water is cyclic as well, or comes from connate waters. The total water is calculated as consisting of three-fourths sedimentary and one-fourth igneous and metamorphic drainage. Similarly, 89 per cent of the sulfate must have derived from rain water. No corrections arise for carbonate and nitrate because the bicarbonate content in rain water is very small and the nitrate content is comparatively small as well.

The content of sulfate in "sedimentary" river water is found to be more than three times the calculated amount which could be produced by weathering. Sulfate deposits, volcanic emanations, and burning of coal are insufficient as sources of the excess sulfate, which is accordingly attributed to the circulation of volatile sulfur compounds, chiefly hydrogen sulfide, from the shallow waters of the sea to the atmosphere and further to the land surface. The hydrogen sulfide is generated by the reduction of sulfates in marine muds, and some is formed, in addition, by the decomposition of organic matter on the continental areas.

MINERAL SPRINGS AND HOT SPRINGS

The water in mineral springs and hot springs differs from ordinary well and spring water either in concentration or in composition or in both. Local conditions play the dominant role in causing these differences. Clarke (1924) classifies these waters according to their principal anion. Consequently, the main types include chloride, sulfate, carbonate, and acid waters. There are, in addition, silicate, borate, nitrate, sulfide, and phosphate waters and waters of mixed character. It is evident that this classification is only approximate and rather flexible.

A noteworthy feature of many mineral springs is their content of appreciable amounts of dissolved gases, many of which are held in the water under pressure, being released upon the emergence of the water onto the Earth's surface. Carbon dioxide, hydrogen sulfide, nitrogen, and inert gases are present in many mineral waters.

Analyses of some more typical waters from mineral wells and springs are given in Table 6.9. The analyses are selected from those recalculated and published by Clarke (1924).

The water of the artesian well at Abilene, Kansas, is a natural brine. Probably many such brines are formed by solution of salts from rock salt beds by percolating waters. However, in some cases thermal waters may intermingle with brines associated with petroleum deposits (Miholić, 1935*a*) or with connate waters. The salinity of natural brines is very high, and sometimes the concentration of some of their constituents may reach appreciable amounts; for example, certain natural brines from Michigan contain up to 10 per cent magnesium. The analyses of mine waters given in Table 6.3 represent waters high in calcium. The sulfate waters have a relatively low salinity, which is due to the low solubility of calcium sulfate. Some of the carbonate and bicarbonate waters are high in calcium, whereas another group contains sodium as the predominating cation. The siliceous waters, especially those of volcanic origin, contain colloidal silica. The analysis of the Big Iron Spring in Table 6.9 represents a nonvolcanic water, whereas that of the Bench Spring is a siliceous geyser water. Two analyses of waters high in nitrates, phosphates, and borates are included in Table 6.9. Free acids, either sulfuric or hydrochloric, present in mineral springs are the result of the oxidation of sulfides or hydrogen sulfide, with the subsequent liberation of hydrochloric acid from chlorides, or of admixture of water of volcanic origin. The water of Devils Inkpot, quoted as an example of the acid waters, is remarkable for its high content of ammonium salts.

A number of minor constituents is present in mineral waters, partly leached out from surrounding rocks and partly derived from volcanic emanations. The therapeutic value of mineral waters is largely based on the presence of such constituents. Intonti (1939) reports the presence of, among others, the following elements in the water of Fonte di Fiuggi in Italy: Sr, Cu, Cr, Ba, Zn, V, Sn, Rb, Ag, Pt, Pb. Strock (1941) gives the analysis of some mineral waters at Saratoga Springs, reproduced in Table 6.10. Strock suggests that the remarkably high content of zirconium is caused by the presence of calcium dicarbonato zirconylate, $\text{Ca}[\text{ZrO}(\text{CO}_3)_2]$, which is stable in the acid Saratoga waters with a pH of 5.5, as is also the corresponding tin compound, whereas the titanium complex is supposed to be stable only in alkaline hot mineral waters.

The juvenile waters or those of deep-seated magmatic origin are

TABLE 6.9
ANALYSES OF MINERAL WATERS

CONSTITUENT	BRINE FROM ARTESIAN WELL, ABILENE, KAN., U.S.A.	SULFATE WATER FROM SPRING NEAR DENVER, COLO. U.S.A.*	ARTESIAN CARBONATE WATER, LA JUNTA, COLO., U.S.A.	SILICIC WATER, BIG IRON SPRING, ARK., U.S.A.	SILICEOUS GEYSER WATER, BENCH SPRING, YELLOWSTONE NATIONAL PARK, WYO., U.S.A	HOT WATER, PARROT SHAFT, SULPHUR BANK, CALIF., U.S.A.†	PHOSPHATE WATER, VIRY, SEINE-ET-OISE, FRANCE	ACID WATER, DEVILS INK POT, YELLOWSTONE NATIONAL PARK, WYO., U.S.A.‡
	Per Cent							
HCl, free. . . .								0 18
H ₂ SO ₄ , free. . .								1 29
H ₂ BO ₃								2 73
Cl	61 63	2 62	4 01	1 27	trace	14 39	5.11	
Br.	0 29			trace				
I.	trace			trace				
SO ₄	0 07	72 56	4 26	3 93	29 22	10.06	7.74	67 66
CO ₃			47 45	41 47		4.73	19.46	
NO ₃				0 23			6.33	
PO ₄				0 03			22.41	
BO ₂				0 64				
B ₄ O ₇						40.09		
Na.	31 57	11 23	40 09	2 38	12.15	28.49	3.32	0.73
K.	trace	0 22	0 38	0 80	2 05	0 84	trace	0 24
Li.		trace	trace	trace	trace		trace	0.01
NH ₄				0 03		0 02		22 85
Ca.	4 85	0 53	0 27	23.54	trace	0.44	30.38	1.18
Sr.				trace				
Ba.				trace				
Mg.	1 52	12 79	0 15	2 56	trace	0 03	1.21	0.36
Mn	trace		trace	0 17				
Fe.				0.10				
Al.		trace						0.10
Fe (ferrous). . .	0 05	trace	0 14			0 01		trace
Fe ₂ O ₃					5 80			
Al ₂ O ₃			0 20					
SiO ₂	trace	0 05	3 05	22 85	50 78	0.90	4 04	2 67
Total.	100 00	100 00	100 00	100.00	100 00	100.00	100 00	100 00
Total salinity (p.p.m.)	178,900	60,584	1,668 3	199	473	4,632	490	3,365

* Contains 210 p.p.m. free CO₂.

† Contains some organic matter, a little H₂S, and a considerable amount of CO₂.

‡ Contains 65 p.p.m. free CO₂ and 5 p.p.m. H₂S.

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usually characterized by a notable content of heavy metals, whereas the concentration of such metals in waters of superficial or vadose origin is low or negligible. Other differences also exist in the composition of juvenile and vadose waters. Behre and Garrels (1943) state that ascending solutions tend to have a lower Ca:Mg ratio than do descending ones. They also suggest that many ore deposits may have been formed by the mixing of ground waters with warm metalliferous juvenile solutions. On the other hand, the formation of supergene metalliferous deposits may be caused by the leaching action of acid waters, which reprecipitate heavy metals in proper surroundings.

TABLE 6.10
CONTENT OF TRACE ELEMENTS IN HAYES AND
ORENDA SPRINGS, SARATOGA SPRINGS,
NEW YORK, U.S.A.

Element	Content (mg/l.)
(Cl).....	(3100 0)
Fe.....	3 93
Ti.....	<0 0016
V.....	<0 0016
Zr.....	0 35
Sn.....	0 032
Mn.....	0.0027
Co.....	0
Ni.....	0 00027
Be.....	0 001

Miholić (1933, 1935b, 1947) has presented an age division for mineral waters, based on the presence of characteristic heavy metals in waters connected with joints and faults which are caused by tectonic movements of varying geological age. The groups with the corresponding orogenic epochs are shown in the accompanying tabulation.

Predominating Heavy Metal	Orogenic Epoch
U and its products of disintegration. . .	Algoman (late Archean)
Ni.....	Keweenawan (Proterozoic)
Cu.....	Caledonian
Sn.....	Hercynian
Zn.....	Older Alpine (Cretaceous and early Tertiary)
Pb.....	Younger Alpine (Miocene)
Hg.....	Recent

Some overlapping occurs among these groups, and, besides these predominating metals, small amounts of other heavy metals may be present in the waters. Because biochemical processes are known to be responsible for the enrichment of metals like uranium, copper, and vanadium, the classification of the waters is restricted only to those of igneous origin.

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The hot springs are of considerable geochemical interest, since they represent the closing stage of thermal activity in volcanic regions. There are three great hot-spring areas in the world, viz., the Yellowstone National Park in Wyoming, U.S.A., another in Iceland, and a third in New Zealand. The hot-spring activity is intimately related to volcanic phenomena, even though the most part of the waters in such springs is of meteoric origin. The hot springs of the Yellowstone area were studied in great detail by Allen and Day (1935), who divided them into three groups: (1) waters with calcium carbonate and bicarbonate in solution, (2) siliceous alkaline waters, and (3) siliceous acid waters, usually containing free acids in solution. Intermediary waters occur between these principal types. The character of the Yellowstone hot springs is largely determined by the amount of ground water and its depth of circulation. The waters of the first group contain calcium carbonate derived from limestone and dissolved as bicarbonate by the action of magmatic carbon dioxide. When these waters emerge into the open air, carbon dioxide is released and calcium carbonate precipitated as travertine. The siliceous alkaline waters are characterized by chlorides and carbonates in solution and by a neutral or alkaline reaction. They also carry notable amounts of colloidal silica. An abundant supply of ground water is necessary for their formation. The acid or sulfate springs contain free hydrochloric or sulfuric acid. They are met where the supply of ground water is limited. On such areas there also occur shallow, turbid springs, containing suspended sulfates. The original chemical composition of the deep-seated emanations from the magma is assumed to be constant. Allen and Day (1935) estimate that only about 13 per cent of the hot-spring waters of Yellowstone is of magmatic origin.

Water is the most important constituent of volcanic gases. Allen and Zies (1923) calculated that the content of water vapor in the fumarole gases of the Valley of Ten Thousand Smokes in Alaska was 98.65–99.85 per cent by volume. This water is largely surface water. Zies (1929) estimated the amount of water vapor exhaled from the Valley as $58.5 \cdot 10^3 \text{ m}^3$ per hour (calculated as water). Foshag (1948) calculates the amount of water vapor emitted by the Parícutín Volcano in Mexico as $16 \cdot 10^3$ tons of water per day, the corresponding amount of lava being 10^5 tons. Also in this case a considerable dilution of magmatic emanations by ground water takes place. An analysis of condensed water from the Kilauea Crater in Hawaii made

by Day and Shepherd (1913) showed the presence of considerable quantities of chlorine, fluorine, and sulfur, a little ammonia, and a trace of titanium. Sodium, potassium, calcium, iron, and aluminum, although present, were thought to have been largely derived by solution from the solidified lava.

Allen and Day (1935) and Fenner (1936) have discussed the chemical changes caused by the ascending thermal waters in the surrounding rocks in Yellowstone Park. Silica and sodium are the most important rock constituents of the issuing waters. Alkali halides are carried in the current of water vapor, and carbon dioxide in the emanations. At the lower limit of the ground water the water vapor condenses, causing the salts to go into solution and subsequently react with adjacent rocks. The presence of carbon dioxide is the cause of the high chemical activity of these solutions. Bases are extracted from the rocks, and alkaline solutions are formed which remove silica in colloidal solution. The excess of alumina remains in clay minerals: beidellite is found in the lower levels, and kaolinite in the uppermost parts of the altered rocks. Kaolinite is known to be formed in acid solutions, whereas beidellite is attributed to alkaline surroundings. Consequently, it is concluded that the thermal waters near the surface are acid and that the alkaline waters occur below, where bicarbonates have neutralized the sulfuric acid, originally formed by the oxidation of magmatic hydrogen sulfide by the oxygen dissolved in the percolating solutions. The most notable reaction between the thermal waters and the adjoining rocks consists of the addition of silica and molar replacement of sodium (and calcium) in the feldspars by potassium.

WATER IN CLOSED BASINS

In semiarid and arid regions, where the amount of precipitation is only moderate or small, the soluble weathering products of rocks remain in the soil or are transported to depressions, where the rate of evaporation is too rapid to allow the accumulation of any considerable body of water. There great quantities of dissolved matter are deposited and finally form alkaline or salt lakes or even dry salt beds. The salt solutions may also seep downward, carrying the mineral matter along. When the soil becomes saturated with the brine, a part of the latter seeps downward, whereas the solutions remaining close to the surface are brought back by capillary action. When the surface becomes dry, salts are deposited thereon, usually consisting of sodium, magnesium, and calcium as sulfates, as well as some bicarbonate.

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The basins devoid of an outlet receive water by streams and rivers. In the continental areas of such internal drainage, permanent reservoirs are formed, containing water which is concentrated by evaporation of incoming river water and has a composition entirely different from that of sea water. Many of the great salt lakes are in a semi-solid state. The composition of the brines in such reservoirs varies according to the local conditions. The salt lakes, the greatest of which is the Caspian Sea, are of considerable geochemical interest. The Dead Sea, Searles Lake and Owens Lake in California, and Great Salt Lake in Utah are discussed in this paragraph as examples of the closed basins. The salt and alkaline lakes are divided, according to Clarke (1924), into the following groups: lakes with chloride waters, characterized mainly by sodium chloride and possibly derived, directly or indirectly, from ocean water; bittern waters, rich in magnesium salts; sulfate waters; and carbonate and bicarbonate waters. There are also gradations between these groups and their subgroups. In general, alkaline lakes are representatives of volcanic areas, whereas saline lakes are connected with sedimentary rocks. In recently formed bodies of water derived from igneous and metamorphic rocks, carbonates are abundant; but, with increasing salinity or concentration, calcium carbonate will be precipitated, followed by gypsum if the supply of calcium is adequate. The resulting brine consists chiefly of chlorides.

THE DEAD SEA

The Dead Sea water is now essentially a bittern, relatively low in sodium and high in magnesium. It thus resembles the brines left over after the extraction of sodium chloride from ocean water. The water is rich in bromine and also in calcium. The amount of sulfate is negligible, and carbonate is nearly totally absent. Two analyses of the Dead Sea water, showing the variation in composition in different parts and at different depths of the lake, are given in Table 6.11, which also shows the rather unusual composition of water of the River Jordan, the main feeder of the Dead Sea. All these analyses are quoted from Clarke (1924).

The source of bromine in the Dead Sea water is believed to be the hot springs near and on the bottom of the Sea of Galilee. Water flowing into this lake contains no detectable trace of bromine, whereas 2 g/ton Br are present in the Jordan water. The present-day total salinity of the Dead Sea water, on an average, is 30 per cent, or nearly ten times as high as that of sea water. The approximate total

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salt content of the Dead Sea is presented in Table 6.12, according to Armstrong and Miall (1946).

When the Jordan enters the Dead Sea, the carbonates and calcium sulfate dissolved in its water are precipitated, and almost exclusively chlorides and bromides are added to the brine. The high content of chlorides and sulfates in the Jordan water is due to leaching from beds of rock salt and gypsum in the near-by strata.

TABLE 6.11
ANALYSES OF DISSOLVED SOLIDS IN DEAD SEA
AND RIVER JORDAN WATER

CONSTITUENT	SURFACE WATER, NORTH END OF DEAD SEA	DEAD SEA WATER AT DEPTH OF 300 METERS, NEAR WADY MRABBA	JORDAN WATER NEAR JERICHO
	Per Cent		
Cl.....	65.81	67.30	41.47
Br.....	2.37	2.72	
SO ₄	0.31	0.24	7.22
CO ₃	trace	trace	13.11
NO ₃			trace
Na.....	11.65	5.50	18.11
K.....	1.85	1.68	1.14
Ca.....	4.73	6.64	10.67
Mg.....	13.28	15.92	4.88
Fe ₂ O ₃ +Al ₂ O ₃			1.45
SiO ₂	trace	trace	1.95
Total.....	100.00	100.00	100.00
Salinity (per cent).....	19.215	25.998	0.770

TABLE 6.12
APPROXIMATE TOTAL SALT CONTENT
OF THE DEAD SEA*

Compound	Amount in 10 ⁶ tons
MgCl ₂	22
NaCl.....	11.9
CaCl ₂	6
KCl.....	2
MgBr ₂	0.98
Mg.....	5.8
K.....	1.05
Br.....	0.85

* Based on material from *Raw Materials from the Sea*, by E. F. Armstrong and L. M. Miall (1946). Courtesy of Chemical Publishing Co., Inc.

SEARLES LAKE AND OWENS LAKE

A number of alkaline lakes are found in California. One of them, the Searles Lake in the Mohave Desert, is now almost dry. This lake also contains salts originally present in the neighboring Owens Lake, which flowed into Searles Lake until evaporation lowered its level. Mud is found on the bottom of the lake below the deposited salts. The solid salts in the lake consist nearly entirely of the following salt minerals:

halite,	NaCl
trona,	$\text{Na}_2\text{H}[\text{CO}_3]_2 \cdot 2\text{H}_2\text{O}$
hanksite,	$\text{KNa}_{22}[\text{Cl}](\text{CO}_3)_2(\text{SO}_4)_9]$
borax,	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
glaserite,	$\text{K}_3\text{Na}[\text{SO}_4]_2$
sulfahalite,	$\text{Na}_6[\text{FCl}](\text{SO}_4)_2]$

The composition of the Searles Lake brine, according to Gale (1938), is given in Table 6.13. The brine is very alkaline, with a pH

TABLE 6.13
TYPICAL ANALYSIS OF SEARLES LAKE BRINE

Component	Per Cent
Total K calculated to KCl	4.70
Remaining Cl calculated to NaCl	16.35
Total CO_2 calculated to Na_2CO_3	4.70
Total SO_3 calculated to Na_2SO_4	6.96
Total B_2O_3 calculated to $\text{Na}_2\text{B}_4\text{O}_7$	1.50
Total P_2O_5 calculated to Na_3PO_4	0.16
Total F calculated to NaF	0.01
Other minor constituents	0.30
 Total salts, approximately	 34.68
Water	65.32
 Total	 100.00

of 9.48. It contains no magnesium and only a trace of calcium, although these metals are found in the mud underlying the salts. The bromine content of the brine is about 0.085 per cent, and its lithium content 0.021 per cent. Lithium is isolated from the brine as crude lithium phosphate, and Searles Lake now supplies this element in approximately half the world's total production. Sodium sulfate, carbonate, and bromide, potassium sulfate, bromine, and borax are also produced from the brine. This lake gives about half the world's total output of borax.

An analysis of the water of Owens Lake is given in Table 6.14, quoted from Clarke (1924). Unlike the semisolid Searles Lake, Owens Lake is an alkaline lake, the waters of which are supplied by the

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Owens River. An analysis of this river, according to Clarke (1924), is also given in Table 6.14. Owens Lake is worked for sodium carbonate and borax.

GREAT SALT LAKE

Great Salt Lake is the main remainder of the former great Lake Bonneville. Like all lakes in the Bonneville Basin, it contains salt water. It is fed by waters flowing largely through areas of sedimen-

TABLE 6.14
COMPOSITION OF DISSOLVED SOLIDS IN OWENS LAKE
AND OWENS RIVER WATER, UNITED STATES

CONSTITUENT	WATER FROM OWENS LAKE, CALIFORNIA	WATER FROM OWENS RIVER AT CHARLIES BUTTE, CALIFORNIA
	Per Cent	
Cl.	25 40	9 49
SO ₄	9 89	15 53
CO ₃	22 70	29 84
B ₄ O ₇	1 89	
NO ₃		0 48
Na	37 83	} 19 83
K	2 09	
Ca		8 92
Mg		3 45
SiO ₂	0 20	12 37
Fe ₂ O ₃		0 09
Total	100.00	100.00
Salinity (p.p.m.)	118,830	339

tary rocks, and its salts are derived from previously deposited salt beds. An analysis of the dissolved salts in the water of this lake and two analyses showing the composition of the water of one of its feeders are given in Table 6.15. The analyses are taken from Clarke (1924).

The composition of Bear River water at Evanston is that of a normal river water in which carbonates predominate. The second analysis shows deep-going changes due to the addition of much sodium chloride. Compared with ocean water, the salinity of water from Great Salt Lake is four to seven times as high. The composition of this water and that of the ocean water is, however, largely similar, with the exception of the lower magnesium, the higher sodium, and the ab-

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sence of carbonates in the lake brine. The carbonates are removed from the lake water because the brine at present is not capable of holding calcium carbonate in solution.

SEA WATER

COMPOSITION OF SEA WATER

The water in the oceans and the adjacent seas forms the most important part of the hydrosphere. The volume of the ocean is calcu-

TABLE 6.15
DISSOLVED SOLIDS IN WATER FROM GREAT SALT LAKE
AND BEAR RIVER, UNITED STATES

CONSTITUENT	WATER FROM GREAT SALT LAKE, UTAH	WATER FROM BEAR RIVER AT EVANSTON, WYOMING	WATER FROM BEAR RIVER NEAR ITS MOUTH, AT CORINNE, UTAH
	Per Cent		
Cl	55.48	2.68	32.36
SO ₄	6.68	5.76	8.16
CO ₃	0.09	52.68	21.53
Na	33.17	} 4.49	} 20.54
K	1.66		
Ca	0.16	23.69	10.12
Mg	2.76	6.86	4.76
Fe ₂ O ₃ +Al ₂ O ₃			2.53
SiO ₂		3.84	
Total	100.00	100.00	100.00
Salinity (p.p.m.) . . .	203,490	185	637

lated as $13,703 \cdot 10^{20}$ ml (Kossinna, 1921) or $13,722 \cdot 10^{20}$ ml (Kalle, 1943), and its mass 14,060 Gg, or, according to Kalle (1943), 14,220 Gg. The water in the oceans is usually divided, according to the depth, into the following zones: (1) shallow waters from 0 to 200 m, coastal areas of relatively shallow depth corresponding to the continental shelves; (2) the relatively small area of depths between 200 and 3,000 m, which corresponds to the continental slope; (3) the extensive oceanic abyss between 3,000 and 6,000 m; and (4) the deeps in excess of 6,000 m, which form a very small part of the ocean floor.

Sea water contains a number of dissolved salts which have escaped adsorption during the cycle of dissolved substances and precipitation

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or crystallization during the geological evolution of the Earth. It is probable that all elements are found in solution in sea water. According to present knowledge, more than fifty elements have been detected in sea water or in marine organisms.

Fundamental research on the chemical composition of sea water was carried out by W. Dittmar in 1884. All available data were summarized by Thompson and Robinson (1932) and by Wattenberg (1938). The concentration of the major constituents of sea water is listed in Table 6.16, which is quoted from Sverdrup, Johnson, and

TABLE 6.16

MAJOR CONSTITUENTS OF SEA WATER*

Ion	Parts per Thousand
Cl ⁻	18 9799
SO ₄ ²⁻	2 6486
HCO ₃ ⁻ ..	0 1397
Br ⁻	0 0646
F ⁻	0 0013
H ₃ BO ₃ ..	0 0260
Na ⁺ ..	10 5561
Mg ²⁺ ..	1 2720
Ca ²⁺ ..	0 4001
K ⁺	0 3800
Sr ²⁺ ..	0 0133

Total dissolved solids 34.4816 parts
per thousand. Salinity 34.325 parts
per thousand.

* Based on material from *The Oceans*, by H. U. Sverdrup,
M. W. Johnson, and R. H. Fleming. Copyright 1942 by Prentice-
Hall, Inc. Used by permission.

Fleming (1942). The concentrations are shown for water of 19.00 parts per thousand chlorinity,² and the constituents listed make up over 99.9 per cent of the known dissolved solid constituents of sea water. The salinity² of the ocean water is generally between 33 and 38 parts per thousand.

The amount of dissolved elements in sea water is colossal. Actually, the oceans contain vast potential supplies even of many trace elements. The relative abundance of elements in sea water differs very pronouncedly from that in igneous rocks. Silicon, aluminum, and iron are present in the sea in very small concentrations. With a

2. The chlorinity of sea water is defined as the total amount (g/kg) of chlorine, bromine, and iodine, assuming that the two last-named elements have been replaced by chlorine. The salinity of sea water is defined as the total of dissolved solids, expressed in g/kg, when all carbonate has been converted to oxide, Br and I replaced by Cl, and all organic matter quantitatively oxidized.

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few exceptions, all the elements have actually been available in larger quantities than those now present in sea water. Consequently, factors must operate in the sea which control the concentration of many elements. One of these factors is solubility: additional quantities of a substance transported to the sea in solution in river water are precipitated if the sea water is already saturated with the compound in question. Physicochemical processes and biological activity also control the concentration and presence of many substances in sea water.

The data given in Table 6.16 are valid for surface water. In deeper layers of the ocean the concentration of bicarbonate and calcium is slightly higher. However, regardless of their absolute concentration, the ratios between the relative concentrations of the major constituents of sea water are virtually constant as a result of continuous circulation and mixing. A few elements which have significance as plant nutrients show changes in their relative concentration, and the amounts of dissolved gases may differ widely, particularly near the surface, owing to the activity of living organisms and interchange with the atmosphere. Minor fluctuations in concentration are met in regions of high dilution with a corresponding low salinity.

Evaporation, precipitation, and the horizontal and vertical movements of the water masses regulate the distribution of salinity in the ocean. The formation and melting of ice may also cause changes in salinity. However, the diffusion of the dissolved salts is extremely slow.

In the biological cycle in the sea, plants use inorganic substances and are, in turn, consumed by marine animals. The metabolic activities of marine organisms, on the other hand, convert the elements to inorganic form, and they are released into sea water. The downward movement causes a continuous impoverishment of the surface layers in inorganic constituents; but the supply is replenished by convection, vertical diffusion, and upwelling of the water masses. The contribution of dissolved material by rivers and by precipitation, as compared with the huge amounts already present in sea water, is insignificant.

The regeneration of the elements participating in the organic processes in the sea is relatively complete. It is probable that the bulk of all organic matter synthesized by the plants returns to solution before the plant remains reach the bottom after their death. In the bottom deposits regeneration still continues by the action of the

bottom fauna and micro-organisms, but the degree of the changes produced depends on the presence or absence of dissolved oxygen, i.e., on the redox potential.

The concentration of all elements known to occur in sea water as dissolved solids is presented in Table 6.17, which is based chiefly on information given by Sverdrup, Johnson, and Fleming (1942) and Harvey (1945). The values are for water of 19.00 parts per thousand chlorinity, and those for the major elements are valid for surface water. The last six elements listed in Table 6.17 are reported in ashes of marine organisms, from which it is concluded that they are also found in sea water; but there is so far no information available showing their concentration therein. The concentration of inorganic carbon is based on that of HCO_3^- ions because carbon dioxide is mostly present in sea water in the form of bicarbonate. Salts of the weak acids H_2CO_3 , H_3BO_3 , H_3PO_4 , H_3AsO_4 , and H_2SiO_3 are found in sea water.

Marine organisms—plants, animals, and bacteria—cause a redistribution of many of the inorganic constituents of sea water. Consequently, sea water cannot be considered exclusively an inorganic system without regard to the marine organisms found therein. Salts may be adsorbed on the surface of living organisms or on their protoplasm. Likewise, colloidal particles may be adsorbed, e.g., ferric hydroxide on diatoms. Some elements, like iodine, are of physiological importance and are concentrated by animals. They are liberated upon the death and decay of the animals and return to the sea. The analyses in Table 8.3 show that the development and re-solution of skeletal structures of marine organisms affect the concentration of the following elements: Ca, Mg, C (as carbonate), S, P, and Si; but in the case of Mg and S the fluctuations are not appreciable because of the great abundance of these elements in sea water. Copper, strontium, and vanadium are reported as essential constituents of certain marine organisms. Some other elements—Co, Ni, Pb, Zn, F, and As—are also found to be concentrated in marine animals, but the question of their physiological importance is still unsettled.

There are two kinds of minor constituents in sea water, viz., those varying widely in their concentration because of their role in marine plants and those which do not show such fluctuations. Many of the elements of the second group are concentrated in marine organisms, together with the elements whose concentration in sea water is too low to allow them to be detected therein. The adsorption of certain

TABLE 6.17

ELEMENTS PRESENT IN SOLUTION IN SEA WATER*
(Dissolved Gases Not Included)

Element	Concentration (g/ton)
Cl.....	18,980
Na.....	10,561
Mg.....	1,272
S.....	884
Ca.....	400
K.....	380
Br.....	65
C (inorganic).....	28
Sr.....	13
(SiO ₂).....	0.01-7.0
B.....	4.6
Si.....	0.02-4.0
C (organic).....	1.2-3.0
Al.....	0.16-1.9
F.....	1.4
N (as nitrate).....	0.001-0.7
N (as organic nitrogen).....	0.03-0.2
Rb.....	0.2
Li.....	0.1
P (as phosphate).....	>0.001-0.10
Ba.....	0.05
I.....	0.05
N (as nitrite).....	0.0001-0.05
N (as ammonia).....	>0.005-0.05
As (as arsenite).....	0.003-0.024
Fe.....	0.002-0.02
P (as organic phosphorus).....	0-0.016
Zn.....	0.005-0.014
Cu.....	0.001-0.09
Mn.....	0.001-0.01
Pb.....	0.004-0.005
Se.....	0.004
Sn.....	0.003
Cs.....	approx. 0.002
U.....	0.00015-0.0016
Mo.....	0.0003-0.002
Ga.....	0.0005
Ni.....	0.0001-0.0005
Th.....	<0.0005
Ce.....	0.0004
V.....	0.0003
La.....	0.0003
Y.....	0.0003
Hg.....	0.0003
Ag.....	0.00015-0.0003
Bi.....	0.0002
Co.....	0.0001
Sc.....	0.00004
Au.....	0.000004-0.000008
Fe (in true solution).....	<10 ⁻⁹

* Partly based on material from the following sources: *Recent Advances in the Chemistry & Biology of Sea Water*, by H. W. Harvey, 1945. Courtesy of Cambridge University Press. *The Oceans*, by H. U. Sverdrup, M. W. Johnson, and R. H. Fleming. Copyright 1942 by Prentice-Hall, Inc. Used by permission.

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TABLE 6.17—*Continued*

Element	Concentration (g/ton)
Ra.....	$2 \cdot 10^{-11}$ – $3 \cdot 10^{-10}$
Ge.....	present
Ti.....	present
W.....	present
Cd.....	present in marine organisms
Cr.....	present in marine organisms
Tl.....	present in marine organisms
Sb.....	present in marine organisms
Zr.....	present in marine organisms
Pt.....	present in marine organisms

elements on living organisms is illustrated by the higher concentration of Cu, Ag, Au, Ra, and U in water rich in plankton.

A small amount of dissolved organic matter is present in sea water. Particulate organic material consists of living and dead marine plants and animals.

Sea water also contains varying amounts of the gases constituting the atmosphere. Oxygen, nitrogen, and carbon dioxide (chiefly as carbonate and bicarbonate ions) form the bulk of the dissolved gases. The surface water is very nearly in equilibrium with the air in regard to oxygen and nitrogen. During the summer, shallow waters are often supersaturated with oxygen. In deep and stagnant waters oxygen is deficient. Ammonia, argon, helium, and neon are also reported as constituents of sea water. Small amounts of hydrogen, hydrogen sulfide, methane, and some other hydrocarbons may sometimes occur in near-shore waters. The amount of the inert gases in sea water seems to vary with the quantity of dissolved nitrogen. The concentration of the more important gases in sea water is presented in Table 6.18. Sea water is nearly saturated with helium and neon.

Sea water is normally alkaline, having a pH between 7.5 and 8.4. Higher values are found in tide pools, bays, and estuaries, in which plants utilize carbon dioxide, whereas in diluted water and in isolated basins, where hydrogen sulfide is generated, the pH may approach neutrality or even fall within the acid region. Variations in the pH of sea water are also caused by the interaction of plant and animal life in the sea. In some cases, when the former is more abundant than the latter and photosynthetic activity thus exceeds the respiration, the pH may approach the value 10. Notable rises in the pH cause the conversion of a part of bicarbonate in sea water to carbonate. When the pH is above 9, magnesium hydroxide may be precipitated, together with calcium carbonate. As a rule, the pH falls with rising

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temperature and pressure. No adequate information is available about the redox potential of sea water.

Regional changes occur in the composition of sea water, mainly connected with the biological activity taking place in the sea. Thus, e.g., the Antarctic is very rich in nitrate and the Pacific in silicate. The concentration of silicate shows seasonal variations caused by diatoms, which utilize silicate. There is, in addition, a close correspondence between the concentration of phosphate and nitrate and the degree of biological activity in the sea. A seasonal variation in the phosphate is found in many places: during the summer the water is nearly totally devoid of these salts. In the deep waters of the open ocean, where phytoplankton does not grow because of the lack of light, a great supply of phosphate is available, formed from the re-

TABLE 6.18
DISSOLVED GASES IN SEA WATER

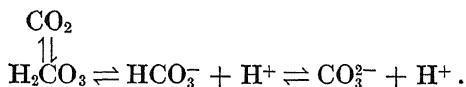
Compound	Concentration (ml/l)
Oxygen.....	0-8.5, or more
Nitrogen.....	8 4-14.5
Total carbon dioxide.....	34-56
"Argon"*.....	0 2-0.4
Helium and neon.....	$1.2 \cdot 10^{-4}$ - $1.8 \cdot 10^{-4}$

* Residue after the extraction of nitrogen.

mains of organisms. Similarly, the deep waters are richer in nitrate than are the surface waters. Diatoms and algae, which utilize nitrate during the summer months, cause a seasonal variation in its quantity.

THE CARBON DIOXIDE SYSTEM IN SEA WATER

The role of sea water as the mechanism regulating the content of carbon dioxide in the atmosphere is, geochemically, of high importance. According to Goldschmidt (1933a), the total quantity of carbon dioxide in the atmosphere is 0.4 g and in sea water 20 g per square centimeter of the Earth's surface. Consequently, the quantity in sea water is about fifty times as high as that in the atmosphere. The chief reason for the stabilization is that the four forms of carbon dioxide in the sea—free carbon dioxide, carbonate and bicarbonate ions, and the undissociated H_2CO_3 molecules—form a buffer system (Wattenberg, 1936). All these forms are in equilibrium with one another and with the hydrogen ions present in solution, as follows:



The free, i.e., unbound and undissociated, carbon dioxide consists of CO_2 and H_2CO_3 molecules in solution and in equilibrium with one another. The total concentration of carbon dioxide is determined by the following equation:

$$c_{\Sigma\text{CO}_2} = c_{\text{CO}_2} + c_{\text{HCO}_3^-} + c_{\text{CO}_3^{2-}}.$$

The carbon dioxide equilibrium depends on all physical, chemical, and biological factors active in the sea. A change in the total concentration of carbon dioxide, caused, for example, by assimilation and respiration, results in a corresponding adjustment of all concentration constants until a new equilibrium is attained. Physical factors, such as changes in temperature and salinity, disturb the equilibrium by causing changes in the equilibrium constants. The effects produced by such means can also be traced outside the phase boundary in the atmosphere and in the solid phases containing carbon dioxide as carbonates. Among the latter, only calcium carbonate has practical importance.

The French chemist, Th. Schloesing, was the first to prove experimentally in 1872 that the solubility of calcium carbonate is a function of the carbon dioxide content of the air in equilibrium with water in the system air-water-calcium carbonate. Schloesing concluded that the sea, owing to its many times higher content of carbon dioxide as compared with that present in the atmosphere, regulates the quantity of carbon dioxide in the latter. However, Krogh (1904b) found that, actually, the tensions of carbon dioxide in the surface layers of the sea and in the atmosphere are of the same degree of magnitude. Later studies by Buch (1939a, b, 1942a) have shown that the atmosphere, as a matter of fact, regulates the tension of carbon dioxide in the sea. The cycle of carbon dioxide between the atmosphere and the sea is discussed in chapter 19, and the formation and solution of calcium carbonate, which forms a part of the carbon dioxide equilibrium in the sea, is treated in chapter 15.

An exchange of other dissolved gases, i.e., certain nitrogen compounds, also takes place between the sea and the atmosphere. Nitrogen compounds in relatively high concentration are present in rain water, and they finally reach the sea either in rainfall or in drainage from the land. At the phase boundary between the atmosphere and the sea they again enter the former geosphere.

DISTRIBUTION OF ELEMENTS BETWEEN SEDIMENTS
AND SEA WATER

Goldschmidt (1932) divided the elements into two general groups according to their distribution between the seas and the continents, viz., into thalassophile and thalassoxene elements. The first group includes chlorine, bromine, boron, sulfur (as sulfates), iodine to a lesser extent, and also sodium. The thalassoxene group incorporates, among others, all such elements as are precipitated in the hydrosphere as a result of the hydrolytic decomposition of their salts, e.g., aluminum, iron, and thorium. The amount of some thalassophile elements, e.g., sodium, has increased during the geological history of the Earth, whereas that of others, like boron probably, has decreased. An equilibrium seems to be attained between the amounts carried to the sea and those removed therefrom in case of still other elements, calcium, for instance.

Sodium, calcium, and magnesium are dissolved during the chemical decomposition of rocks and are transported to the sea, whereas potassium is largely retained in clays. The values presented in Table 6.16 show that, in sea water, sodium and magnesium predominate among the cations in solution, whereas the concentration of potassium is small. The low concentration of calcium is due to the deposition of this metal in the carbonate sediments.

If the total amount of igneous and metamorphic rocks weathered during the geological evolution of the Earth is known and if the actual amounts of the elements in sea water are known in addition, the quantity of each element which has been transported to the sea through the weathering processes can be calculated. However, only a part of the dissolved substances has remained in solution. Joly (1899) has shown that approximately 600 g of average igneous rock must be weathered in order to produce the necessary sodium now found in 1 kg of sea water, provided that one-third of the sodium in the parent-rocks is retained in the sediments and that two-thirds are still present in the ocean. A similar result was that obtained by Goldschmidt (1933*a*) (see chap. 5), who calculated that approximately 160 kg of rock to every square centimeter of the Earth's surface has weathered, producing 278.11 kg sea water per square centimeter. Thus $0.575 \text{ kg} \cdot \text{cm}^{-2}$ rock has been weathered to produce 1 kg of ocean water. Calculations showing the geochemical balance of some elements in sea water were carried out by Goldschmidt (1933*a*,

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1937a). The balances presented in Table 6.19 are calculated from Tables 2.3 and 6.17, assuming that 600 g average igneous rock are weathered for each kilogram of ocean water.

Among the alkali metals, only sodium is noticeably transferred to sea water, whereas the others are retained in clays. Because living or-

TABLE 6.19
GEOCHEMICAL BALANCE OF SOME ELEMENTS IN SEA WATER

Element	Total Amount Supplied to Sea Water (g/ton)	Amount Present in Sea Water (g/ton)	Transfer Percentage
Li.....	39	0.1	0.3
B.....	1.8	4.6	256
C.....	192	28	14.6
N.....	27.78	0.7	2.5
F.....	540	1.4	0.3
Na.....	16,980	10,561	62
Mg.....	12,540	1,272	10
Al.....	48,780	1.9	0.004
Si.....	166,320	4	0.002
P.....	708	0.1	0.01
S.....	312	884	283
Cl.....	188.4	18,980	10,074
K.....	15,540	380	2.4
Ca.....	21,780	400	1.8
Sc.....	3	0.00004	0.001
V.....	90	0.0003	0.0003
Mn.....	600	0.01	0.002
Fe.....	30,000	0.02	0.00007
Co.....	13.8	0.0001	0.0007
Ni.....	48	0.0005	0.001
Cu.....	42	0.011	0.03
Zn.....	79.2	0.014	0.02
Ga.....	9	0.0005	0.006
As.....	3	0.024	0.8
Se.....	0.054	0.004	7.4
Br.....	0.972	65	6,687
Rb.....	186	0.2	0.1
Sr.....	180	13	7.2
Y.....	16.86	0.0003	0.002
Mo.....	9	0.0007	0.008
Ag.....	0.06	0.0003	0.5
Sn.....	24	0.003	0.01
I.....	0.18	0.05	28
Cs.....	4.2	0.002	0.05
Ba.....	150	0.05	0.03
La.....	10.98	0.0003	0.003
Ce.....	27.66	0.0004	0.001
Au.....	0.003	0.000008	0.3
Hg.....	0.3	0.00003	0.01
Pb.....	9.6	0.005	0.05
Bi.....	0.12	0.0002	0.2
Ra.....	0.00000078	$3 \cdot 10^{-10}$	0.04
Th.....	6.9	<0.0005	<0.007
U.....	0.6	0.0016	0.3

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ganisms collect and concentrate potassium from the ocean water, they may increase the rate of removal of this metal from solution. Among other elements listed in Table 6.19, calcium, aluminum, silicon, iron, and manganese are largely removed from sea water. The present concentrations of chlorine, bromine, sulfur, and boron in sea water are higher than those calculated from the amounts actually transported into the sea. Boron and sulfur are, in addition, noticeably bound in marine sediments, and therefore the quantities of these elements actually added to the sea are still greater in proportion. Thus these four elements must also be added to the sea by volcanic emanations and juvenile waters, and the primordial atmosphere of the Earth must have contained volatile compounds of these elements, which were accumulated in the primeval ocean (Goldschmidt, 1937b).

Considerable amounts of sodium, potassium, magnesium, calcium, strontium, carbon, nitrogen, selenium, and iodine, which form relatively easily soluble compounds, remain in sea water in quantities exceeding 1 per cent of the potential supply. They crystallize out finally in the evaporate sediments. It is important to note that the greatest part of many elements like mercury, copper, arsenic, and lead are removed with the hydrolyzate and oxidate sediments and thus do not remain in sea water. This phenomenon is called depoisoning of sea water, and it is of great importance for the existence and maintenance of life in the seas.

CYCLE OF DISSOLVED SUBSTANCES

The principles of the cycle of matter in Nature were presented in chapter 5. The total cycle is divided into two parts: the minor cycle and the major cycle. The former forms a small closed part within the total cycle. On previous occasions the cycle was discussed without attention to the form of matter participating in it. With special reference to the hydrosphere, the cycle of matter in solution is of importance. In this cycle the matter migrates either as dissolved substances or as hydrosols.

A perpetual cycle of water exists in Nature, consisting of evaporation, precipitation, and drainage. Dissolved substances and hydrosols participate in this cycle, and their migration in the hydrosphere forms a part of the minor cycle. Their cycle is presented in Figure 6.1. Two important inorganic sources of matter are present in this cycle, viz., chemical decomposition and volcanic emanations. By the

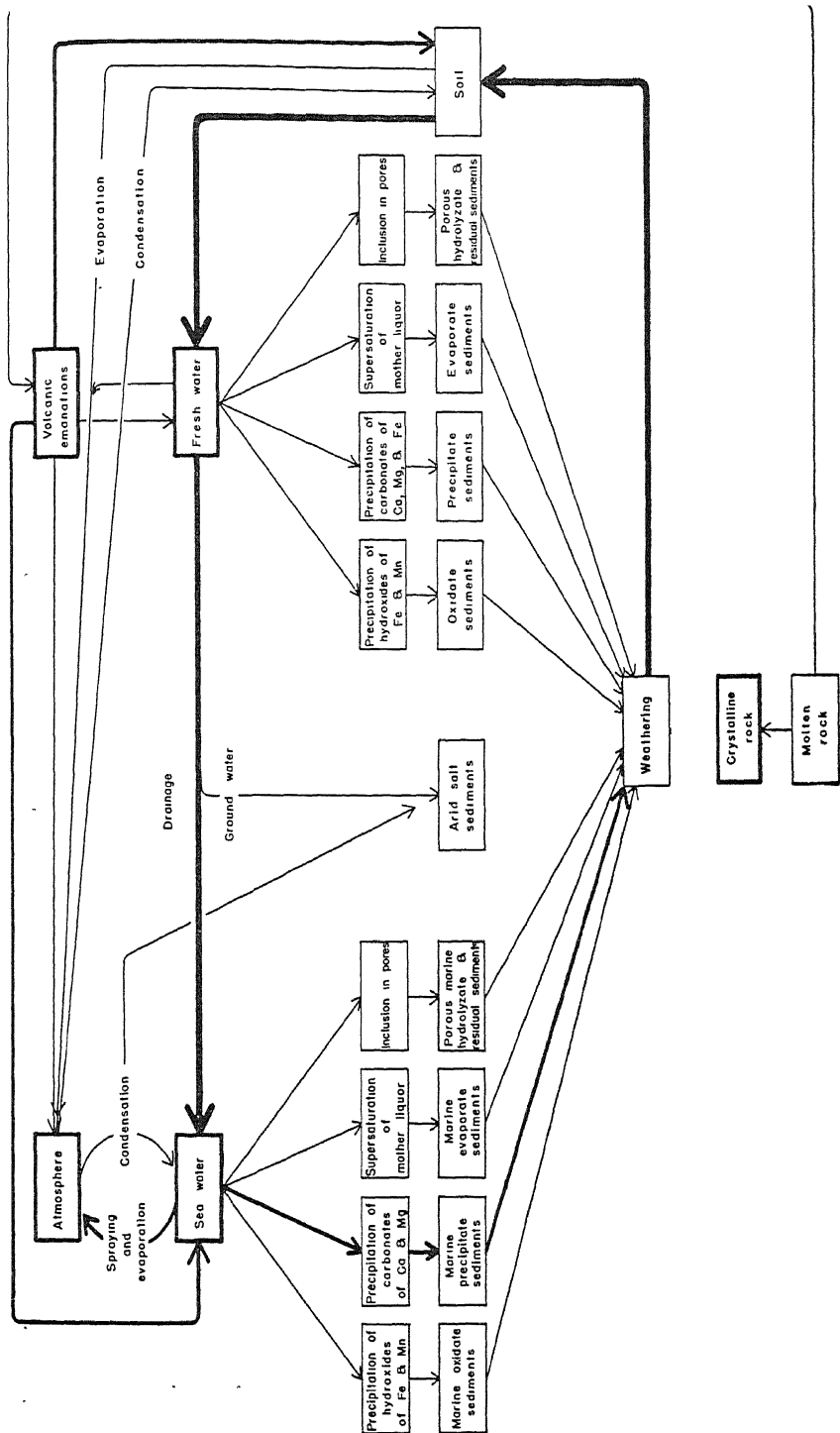


Fig. 6.1.—The cycle of dissolved substances

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former process the minerals of solid rocks are brought into solution, whereas the volcanic emanations release their burden directly into the atmosphere and hydrosphere and partly into the soil. The solutions formed by the action of weathering processes deposit a part of their contents in fresh-water sediments, whereas another part is transported to the sea, becoming partly separated in marine sediments and partly remaining, for long periods of geological time, in sea water.

Rock debris is also carried by the rivers, along with dissolved and colloidal substances. A considerable proportion of the particulate matter is already deposited as near-shore sediments, and the finely divided material is largely coagulated and settles down when brought into contact with salt water. Physicochemical processes may take place between the particles and the sea water, some of which may affect the composition of the dissolved substances. However, such changes will be exceedingly slow, because the annual total of dissolved solids carried by rivers ($2.735 \cdot 10^9$ tons) is only a negligible part of the total of the dissolved solids in sea water, which is $4.619 \cdot 10^{16}$ tons. This small quantity is probably entirely removed from solution. The reactions comprise the solution of the constituents of the debris, adsorption on the particles, ionic exchange between the particles and sea water (e.g., between potassium and the clays), and interaction between sea water and the particles, leading to the formation of new substances (e.g., glauconite, phillipsite, feldspar, and clay minerals). Halmyrolysis is used as a group name for such reactions (see chap. 33). By these reactions ions may be removed from sea water which would not otherwise be precipitated. However, many questions relating to changes in the composition of sea water by such reactions are still unsolved.

Parallel to the cycle described above runs another cycle of minor importance. Substances present in sea water are transferred to the atmosphere by the action of surf and spraying not only along the coasts but also in the open ocean. The greater part of these contaminants is returned to the sea by precipitation, whereas another part is transported by the wind over long distances, brought to the surface of the Earth by precipitation, and finally returned to the sea. In arid regions substances may also be directly carried from the atmosphere to the Earth's surface, where they remain as insoluble deposits because of the small amount of precipitation. It has been suggested that this might have been the origin of the Chilean nitrate

deposits. As was pointed out in a previous paragraph, the evaporation of ground water in arid regions may cause the separation of salts on the Earth's surface.

The formation of oxidates, precipitates, and evaporates in seas and lakes is due to the fact that the solubility product is exceeded, to geochemical sorption, to removal of the solvent by evaporation, or to the action of organisms. There is, in addition, still another process responsible for the removal of dissolved substances from natural waters. During their formation the porous hydrolyzate and oxidate sediments incorporate considerable amounts of water in their pore space. The compounds dissolved therein will thus become inclosed in the sediments (formation of connate waters). Quantitatively, this process is not very important, but in some instances it affords a possibility of deciphering the origin of the sediments. It must also be accounted for when investigating the geochemistry of elements which are typical of marine hydrolyzate sediments, like the thalassophile boron.

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STRUCTURE OF THE ATMOSPHERE

THE atmosphere is the outermost of the geochemical spheres of the Earth. It consists of a mechanical mixture of a number of gases and vapors. Its upper limit is, so far, unknown. Spectrographic investigation of the aurora borealis proves the presence of nitrogen and oxygen even at a height of 1,000 km. At still greater heights the atmosphere gradually thins out into the practically empty interplanetary space above. The upper limit is set where the gas molecules no longer follow the Earth in its movement along its orbit. Russell and Menzel (1933) showed that collisions between hydrogen and helium and metastable oxygen atoms in the upper atmosphere would give the former two atoms velocities exceeding the escape velocity from the gravitational field of the Earth, whereas the heavier atoms, such as nitrogen, oxygen, and neon, would remain in the atmosphere. Free oxygen in the atmosphere is essential for the whole process.

The atmosphere is in contact with the lithosphere and the hydrosphere. Air penetrates the spaces between the soil particles, and consequently the presence of oxygen, carbon dioxide, and water vapor gives rise to a number of important reactions in the biosphere. In the upper lithosphere atmospheric gases may occur in pores of rocks. The lower limit of the atmosphere is determined by the depth of caves, mines, and bore holes. In volcanoes the atmospheric gases are mixed with gaseous emanations. Additions to the atmosphere are also derived from the gases in the microscopic and larger cavities in rocks, occluded gases, the great subterranean reservoirs of petroleum gases, and from the gases dissolved in the water of mineral springs and wells. Biochemical processes in the biosphere produce large quantities of gases, e.g., oxygen, nitrogen, carbon dioxide, and methane. The gases connected with igneous activity are discussed in chapter 5 and the other natural gases in chapter 8.

The lowermost part of the atmosphere, up to the height of approximately 11 km, is called the troposphere. It is the convection region, and the atmospheric phenomena take place therein. The next overlying layer is called the stratosphere. It is characterized by an approximate constancy of temperature. It is, in turn, followed by the ionosphere, which has a lower limit at a little less than 100 km over the Earth's surface and continues up to the outer limits of the atmosphere. The ionosphere is an ionized layer. The radio waves are reflected therein by two layers: Region E, called the Kennelly-Heaviside layer, at approximately 76 or 84 km over the surface, and Region F, the Appleton layer, at a height of 250 km. Free electrons are present in these two layers. In the E layer the air is warmed and ionized by the absorption of certain solar radiations of short wave length.

The main features of the structure of the atmosphere are shown in Figure 7.1. The information concerning the structure and properties of the upper atmosphere has largely increased with the use of the high-altitude jet-propulsion rockets for atmospheric research. There are new indications of the further division of the F layer into two separate layers, F_1 and F_2 , situated around 200 and 300 km, respectively.

In the lower stratosphere the temperature is low, but up to a height of about 160 km there are indications of a slow increase in temperature. According to Seaton (1947), high temperatures are to be expected at E-layer heights of 100 km, whereas the F_1 and F_2 layers may again be at low temperatures. It has been assumed that the temperature in the highest parts of the Earth's atmosphere lies around 1,000° C.

A warm ozone layer exists in the stratosphere approximately between the heights of 30 and 60 km. It is called the ozonosphere. The maximum ozone concentration is met at a height of approximately 40 km. The existence of the ozonosphere is caused by the absorption of the ultraviolet radiation of the Sun in these strata, which also results in an increase in the temperature in the ozonosphere.

In its present cool stage the Earth is able to maintain an atmosphere. However, if it once was hot on the surface, it must have lost all its hydrogen and helium and most of the other gases constituting the primordial atmosphere. The separation of the atmophile elements was first discussed by Goldschmidt (1923), who listed hydrogen, nitrogen, the inert gases, and probably also chlorine as typically at-

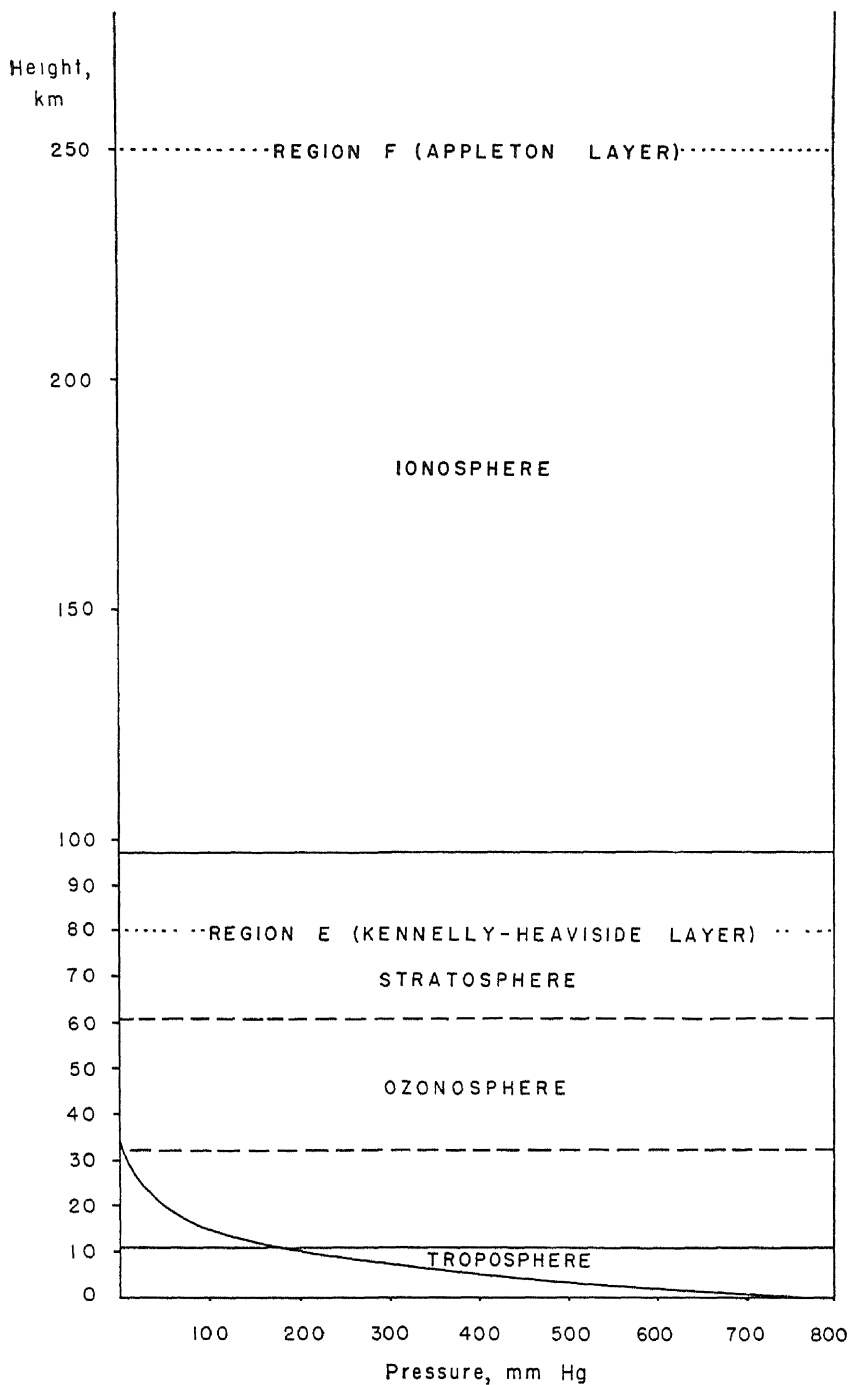
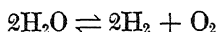


FIG. 7.1.—The structure of the atmosphere

mophile elements. Actually, it is possible that all the atmophile elements—including also carbon as dioxide and some others, like sulfur, selenium, tellurium, arsenic, chlorine, bromine, and iodine, which are easily volatile or whose compounds with hydrogen have this property—escaped from the primeval atmosphere. Mercury might, at least partly, have shared their fate. The escape of the atmophile elements must have taken place during the necessarily short time when the primitive Earth was still very hot (surface temperature above $8,000^{\circ}\text{K.}$) and the rates of escape were rather fast. According to Russell and Menzel (1933), the conclusion seems to be unavoidable that most of the loss occurred during the first few years, if not the first few days, of the Earth's existence as an independent body. The loss of hydrogen must have been practically immediate.

The rapid cooling stopped the escape and left an atmosphere in which neon is less abundant than argon. According to the explanation of the origin of the atmosphere, most, if not all, of the original supply of nitrogen and oxygen was lost and likewise all helium, free hydrogen, and water vapor. Consequently, the hydrosphere and most of the present atmosphere were probably formed by volcanic emanations escaping from the lithosphere after the solidification of the Earth's crust. The investigations of Lord Rayleigh (1939) showed that igneous rocks contain about fifty times as much nitrogen as does the atmosphere. The values presented in Table 2.3 show that nitrogen is actually one of the more abundant elements in the upper lithosphere.

The origin of oxygen in the Earth's atmosphere has been and still is the subject of controversial theories. Tammann (1924*b*) suggested that all or most of the free oxygen originated through thermal dissociation of water vapor before a solid crust of the Earth was formed, when the temperature of the primordial atmosphere was still above $1,500^{\circ}\text{C.}$ The hydrogen formed in the reaction



was thought to dissipate into space at a rapid rate. Goldschmidt (1933*a*) criticized Tammann's ideas and pointed out that during the geological evolution of the Earth much of the oxygen became fossil, being consumed in the oxidation processes at and near the surface. According to Goldschmidt, it might also be possible that free oxygen is constantly formed in the atmosphere as the result of a photochemical disintegration of water vapor and that

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the hydrogen released in this reaction can, even under the present atmospheric temperatures, dissipate into the void. Goldschmidt further emphasized the importance of the photosynthetic decomposition of carbon dioxide by chlorophyll-bearing plants, whereby oxygen is generated. If all fossil oxygen and that now present in the Earth's atmosphere is produced from carbon dioxide by the physiological activity of green plants, an average content of 0.11–0.17 per cent of carbon, essentially as coal and bitumen, should be present in sedimentary rocks. The calculated average is of the right degree of magnitude and consequently affords positive proof of the assumption that the atmospheric oxygen has been produced, entirely or largely, from carbon dioxide.

According to Wildt (1940), there can be no doubt that Tammann's process has been instrumental in producing the initial supply of free oxygen needed by the first breathing organisms.

However, it is now known that carbon dioxide in the troposphere is prevented from being decomposed photochemically by the protective ultraviolet absorption of the vast mass of oxygen in the upper atmosphere. Unsöld (1941) has shown that the cosmic abundance of neon is as high as that of oxygen and nitrogen. This result seems to afford proof of the loss of neon from the Earth's original atmosphere. Consequently, it may be concluded that water vapor from the original atmosphere must also have escaped nearly quantitatively and that the water found in the present hydrosphere is of juvenile origin. If the mass of the primeval hydrosphere had been smaller than that of today, less oxygen would have been obtained from the thermal dissociation of water vapor if Tammann's theory is accepted. According to Wildt (1942a), the great abundance of carbon dioxide and the absence of water in the atmosphere of Venus may suggest that the quantity of juvenile water given off during the geological evolution of the Earth has not been of the same order of magnitude as the present-day total mass of the hydrosphere.

COMPOSITION OF THE ATMOSPHERE

In 1779 the Swedish chemist, Karl Wilhelm Scheele, reported the results of the first systematic study of the composition of the atmosphere over a considerable period of time. The most recent analyses give the average composition for the atmosphere, presented in Table 7.1, chiefly according to Paneth (1939). The total mass of the Earth's atmosphere is estimated to be 51.3 Gg. The weight of the

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atmospheric gases per square centimeter of the Earth's surface is 1.003 kg, of which the geochemically most important constituents comprise the following amounts (Goldschmidt, 1933a):

Constituent	$\text{g}\cdot\text{cm}^{-2}$
Nitrogen.....	755
Oxygen.....	230
Carbon dioxide .	0.4
Total.....	985.4

Table 7.1 also shows the masses of the atmospheric constituents (Humphreys, 1940). The percentage figures probably present the average composition of the air not only in the troposphere but also in the lower layers of the stratosphere. Because the absolute amount

TABLE 7.1
AVERAGE COMPOSITION OF THE TROPOSPHERE (DRY AIR)
(Mass of the Total Atmosphere and Its Constituents)*

Compound	Percentage by Weight	Percentage by Volume	Total Mass (Gg)
Total atmosphere....			51.3
Dry air	100.00	100.00	51.17
Nitrogen	75.51	78.09	38.648
Oxygen.....	23.15	20.95	11.841
Argon.....	1.28	0.93	0.655
Water vapor	variable	variable	0.13
Carbon dioxide.....	0.046	0.03	0.0233
Neon.....	0.00125	$1.8\cdot 10^{-3}$	0.000636
Krypton.....	0.00029	$1\cdot 10^{-4}$	0.000146
Helium.....	0.000072	$5.24\cdot 10^{-4}$	0.000037
Xenon.....	0.000036	$8\cdot 10^{-6}$	0.000018
Hydrogen.....	0.000003	$5\cdot 10^{-5}$	0.000002
Ozone†.....	0.000002	$1\cdot 10^{-6}$	0.00003
Radon‡.....	$4.52\cdot 10^{-17}$	$6\cdot 10^{-18}$	$232\cdot 10^{-19}$

* Partly based on material from *Physics of the Air*, by W. J. Humphreys. Copyright 1940. Courtesy of McGraw-Hill Book Co.

† Variable; increases with height.

‡ Variable; decreases with height.

of the atmospheric constituents in the upper stratosphere is very low, the percentage composition given in Table 7.1 remains practically constant therein, even though some changes in the relative proportions of the gases might occur (Lepape and Colange, 1935). Although the content of oxygen decreases with increasing height, the $\text{O}_2:\text{N}_2$ ratio remains rather constant. According to Whipple (1942), there is indirect evidence that the atmosphere in the region from 60 to 88 km above sea level has a mean molecular weight similar to that at the Earth's surface.

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Along with the constituents listed in Table 7.1, the atmosphere contains water vapor in amounts varying from 0.02 to 4 per cent by weight. The content diminishes rapidly with increasing height. The amount of water vapor also depends on temperature. It is known that the percentage of water vapor in the lower atmosphere decreases from the equator toward the poles. The annual average values, given by Humphreys (1940) according to J. von Hann and R. Süring, are given in Table 7.2. Other constituents include carbon monoxide, considerable quantities of which may be present in city air. Formaldehyde, $\text{H} \cdot \text{CHO}$, identified by Dhar and Ram (1933) in rain water, is believed to result from the reaction

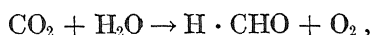


TABLE 7.2
CHANGES IN THE COMPOSITION OF AIR ACCORDING TO LATITUDE

LATITUDE	NITROGEN	OXYGEN	ARGON	WATER VAPOR	CARBON DIOXIDE
	Per Cent by Volume				
Equator	75.99	20.44	0.92	2.63	0.02
50° N.	77.32	20.80	0.94	0.92	0.02
70° N.	77.87	20.94	0.94	0.22	0.03

which is activated by the short-wave ultraviolet radiation of the Sun. The nitrogen oxides, N_2O and N_2O_5 , and one of the heavy waters, HDO , were identified by Adel (1939, 1941*a, b*) as permanent constituents of the atmosphere. The amount of HDO is exceedingly minute. The nitrogen oxides are probably formed by the irradiation of the nitrogen-oxygen mixtures by short-wave ultraviolet radiation. The nitrous oxide forms a layer comparable with the ozone layer; its amount in the atmosphere is several mm-atm (Adel, 1939). Small amounts of nitrogen dioxide, NO_2 , are found in addition, formed by electrical discharges during thunderstorms. The oxidation of nitrogen is a large-scale process, but apparently the oxides are rapidly destroyed. It might be possible that certain simple organic compounds are also synthesized and decomposed by electrical discharges in the atmosphere. Edgar and Paneth (1941) have measured NO_2 contents varying from less than $0.05 \cdot 10^{-6}$ to $2.0 \cdot 10^{-6}$ per cent by volume in the atmosphere. Of similar origin are hydrogen peroxide, H_2O_2 , small amounts of which are found in the air, and ozone, O_3 . Most of

the ozone is situated in the ozone layer, where it is constantly being synthesized by the ultraviolet radiation of the Sun. It is carried down by vertical air currents and finally disappears by chemical decomposition. In the presence of water vapor, ozone is decomposed to oxygen. Consequently, the ozone molecules exist only in the isothermal region (stratosphere), where the H_2O content is extremely small. According to Edgar and Paneth (1941), the concentration of atmospheric ozone varies from $0.5 \cdot 10^{-6}$ to $4.5 \cdot 10^{-6}$ per cent by volume. The sulfurous compounds of the air, viz., sulfur dioxide, SO_2 ; trioxide, SO_3 ; and hydrogen sulfide, H_2S , originate from volcanic emanations, decomposition of sulfur-bearing organic substances, burning of coal, and smelting of sulfide ores. Ammonia is produced by the decomposition of organic nitrogenous substances. Iodine is present in the air in a concentration varying from 0.0001 to 0.001 $\text{mg} \cdot \text{m}^{-3}$. Migeotte (1948) has established the presence of methane, CH_4 , in the Earth's atmosphere. Radon in the atmosphere is the opposite of ozone. It is produced in the Earth's upper crust, as is also helium, and is carried upward in the atmosphere by convection. Its content decreases rapidly with height, and finally it disappears altogether by radioactive decay.

Contrary to the previous belief, the content of carbon dioxide in the air does not decrease with height (Lepape and Colange, 1935; Shepherd, 1936). At a height of approximately 21.5 km, the content, 0.029 per cent by volume, is still identical with that usually present in ground-level air, viz., 0.03 per cent. Haldane (1936) gives 0.021 and 0.044 per cent as limits in country air. However, a quantity corresponding to that of the oxygen consumed is produced by the combustion of fuels and by respiration. As much carbon dioxide as 0.1 per cent by volume was found by Haldane in soil air near the surface, and the range in London air was 0.0425–0.09 per cent, with an average of 0.065 per cent by volume. On the other hand, assimilation diminishes the concentration of carbon dioxide to an extent corresponding to the increase in oxygen. Still another factor regulating the carbon dioxide content of the air is the equilibrium between the sea and the atmosphere (see chap. 19).

If the upper levels of the atmosphere are fairly still, there must begin, under the influence of gravitation, a diffusive segregation of the light and heavy constituents (Paneth, 1939). Consequently, the gases of low specific gravity, such as helium, should be concentrated in the uppermost layers of the atmosphere. The figures given by

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Paneth (1939) show that a separation of the light gases from the heavy ones by diffusion begins to be detectable at a height of about 20–30 km. Glückauf and Paneth (1945) state that the region in which the separation comes fully into action must be above 25 km. The content of helium and oxygen at the Earth's surface is $5.24 \cdot 10^{-4}$ and 20.95 per cent by volume, respectively, whereas the content of helium at the height of 25 km is $5.35 \cdot 10^{-4}$ per cent by volume; that of oxygen at about 21.5 km, 20.895 per cent (Shepherd, 1936); and at 28–29 km, 20.39 per cent (Paneth, 1939). Consequently, there seems to be, somewhere in the stratosphere, a region where helium becomes enriched and oxygen depleted, but up to 25 km the helium content is very nearly the same as near the surface, although a consistent helium surplus is present above 20 km. The results of Glückauf and Paneth (1945) show that no changes occur in the helium content of the air over almost the entire surface of the Earth.

There is no regular change in the composition of the air as a function of the height in the lower atmosphere, and it is unlikely that the gravitational separation continues proportionally to further increase in height because helium has not been observed at the height of 1,000 km in the auroral spectra. However, the absence of helium might be the result of its dissipation into the void if there is an increase of temperature in the upper atmosphere. Because the velocity of escape from the gravitational control of the Earth is $11.2 \text{ km} \cdot \text{sec}^{-1}$ and the mean molecular velocity at 0° C. is $1.84 \text{ km} \cdot \text{sec}^{-1}$ for hydrogen and less for all other gases, the Earth should be able to retain its present atmosphere if the temperature of the upper atmosphere is not too high. There is no evidence indicating that the heavier gases would have been lost since the cooling of the Earth approximately to its present temperature. Yet there is conclusive evidence that the Earth is actually slowly losing helium, if the amount of helium generated during the geological history of the Earth by radioactive decay is compared with that present in the atmosphere.

It has been previously assumed that hydrogen is concentrated in the uppermost parts of the atmosphere. However, no hydrogen is present at 21.5 km height (Shepherd, 1936), and spectrographic evidence shows that the uppermost atmosphere does not consist of pure hydrogen.

The effect of the activities of man on the composition of the atmosphere is geochemically of much importance, because increasing amounts of carbon monoxide and dioxide are released into the at-

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mosphere as a result of the combustion of coal, petroleum derivatives, and other carbonaceous fuels, and by fermentation. The effect caused thereby is discussed in chapter 19. Other substances resulting from these activities, such as sulfur dioxide and trioxide, are of only local importance, with the possible exception of the radioactive substances released by atomic fission.

ATMOPHILE CHARACTER OF ELEMENTS

The elements which are notably enriched in the atmosphere are called atmophile. This group, as listed in Table 4.3, includes hydrogen, carbon (as carbon dioxide), nitrogen, oxygen, and the inert gases. These elements form the bulk of the atmosphere. It must be pointed out, however, that only the inert gases and nitrogen are typically atmophile. The former are chemically highly inert and are consequently found only as free gases in Nature. When found in the lithosphere and the hydrosphere, they occur only as gaseous inclusions or trapped in crystal structures. Nitrogen, on the other hand, appears to be mainly in chemical combination in rocks (Lord Rayleigh, 1939). However, it is not very likely to combine with other elements and accordingly is concentrated, for its greatest part, in the atmosphere. Oxygen is also enriched in the atmosphere, but the amount present therein is very small as compared with the huge amounts bound within the lithosphere and the hydrosphere. In spite of the concentration of oxygen in the atmosphere, its atmophile character is not very pronounced.

According to Goldschmidt (1933b), the halogens chlorine, bromine, and iodine, which might have escaped from the primordial atmosphere, are also included in the atmophile group of the elements. In any case the concentration of these elements in the present atmosphere is too low to allow them to be called atmophile in the proper sense of the word.

The cycle of the atmophile elements will be presented in connection with the discussion of their geochemistry in Part II of this book.

TEMPORARY CONSTITUENTS OF THE ATMOSPHERE

A certain amount of matter, other than the gaseous constituents of the atmosphere, is always present therein, causing the constant impurity of the air in the troposphere. This matter consists of inorganic and organic constituents and organisms.

Meteors of varying size are constantly piercing the atmosphere.

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They lose fine particles and are oxidized by the friction against the air blanket during their flight, whereby meteoritic dust is formed, which finally settles down to the surface of the Earth. According to Nünninger (1940), the contribution of meteoritic dust is greater than was earlier believed, amounting to several thousand grams per square kilometer annually.

Volcanic eruptions and explosions may throw considerable quantities of finely divided material high into the atmosphere. The classical example is the explosion of the Volcano Krakatao in Sunda Strait in 1883, in which volcanic dust was thrown to a height of 40 km into the air. This resulted in meteorological phenomena discernible the world over for a period of several months after the explosion.

Very considerable amounts of dust are present semipermanently or temporarily in the atmosphere. Winds transport much material, such as sand, volcanic ash, dry soil, and dust, especially from semi-arid and arid regions. The total volume of dust in the atmosphere, according to Humphreys (1940), is roughly equal to a cube with 179 meters on the side. Mildner and Röttschke (1935) have found up to 23,500 dust particles of a diameter of $2.5 \cdot 10^{-5}$ to $2 \cdot 10^{-3}$ cm in a liter of air, the highest numbers being caused by industrial activity and fires. However, the number of the particles decreases very rapidly with height.

When deposited, the wind-borne material may account for a considerable contribution of material, e.g., to the ocean-bottom sediments. The great dustfall in southeastern Europe between April 26 and 29, 1928, brought down more than $3.5 \cdot 10^6$ tons of dust; the quantity of dust per square kilometer varied from 4 to 59 tons (Stenz, 1930). Such amounts are not without geochemical importance because they may modify the composition of precipitation and that of soil, river water, etc. Many colored rains and snowfalls are due to dust brought down by precipitation.

Because of the lifting and carrying capacity of the winds, plants, animals, and their products may also be temporarily suspended in the atmosphere. The quantity of such matter is high in summer and low in winter and decreases with increasing height.

The activity of man in contaminating the atmosphere is of much geochemical importance. In cities and in the environs of industrial districts the amount of dust and soot in the atmosphere may be considerable. A maximum fall of 114.05 tons of dust per square mile per month for 1943-47 is reported for Chicago, and the soot content of

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the dust attained a maximum of 26.70 tons per square mile per month (Chambers, 1948). The maximum dustfall per month for the period 1945-47 in Los Angeles was 42.1 tons per square mile (Rich, 1948). These values show the higher degree of contamination in the coal-burning Middle West of the United States, as compared with the oil-burning Pacific Coast. Considerable quantities of arsenic, germanium, and other elements present in coal ashes (see Table 8.5) are thus deposited on the Earth's surface as a result of the combustion of coal. This process forms a definite part in the geochemical cycle of these elements. In like manner vanadium and other trace metals found in petroleum and those added to some petroleum products, e.g., lead in gasoline, are distributed by meteorological processes.

RAIN WATER

The most important geochemical feature of the atmosphere is the fact that oxygen and water vapor present therein cause the chemical disintegration of rocks and their minerals on the Earth's surface. Dry oxygen is comparatively inert, but in the presence of water vapor its reaction rate increases. There is a continuous cycle of water from the hydrosphere to the atmosphere and back to the former either directly by precipitation or indirectly by drainage. This cycle also includes a transport of salts from sea water, called cyclic salts.

During the condensation of water vapor evaporated from the hydrosphere, the salts present in the atmosphere, together with oxygen, carbon dioxide, and nitrogen compounds, dissolve in rain water and thus come into contact with weathering rocks. Other substances become dissolved from the surface of the Earth and increase the decomposing power of water. The rain water acts, accordingly, as an effective carrier of substances which promote chemical denudation in transporting them to the surface of the Earth and distributing them into the weathering rocks. Rain water has a direct solvent action on minerals and rocks, but its action is also indirect. Notable amounts of dissolved solids are lifted up from sea water into the air by the action of spray and surf, and thus the salts of sea water follow through the cycle of water. Their presence in many instances increases the reaction rate of rain water.

Both inorganic and organic matter is dissolved in rain water. Particulate matter is also often present, especially near cities. The most important of the dissolved inorganic constituents are chlorides, sulfates, nitrates, and nitrites of sodium, potassium, calcium, and mag-

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nesium. In addition, nitrogen in the form of free ammonia is present, as is also organic albuminoid ammonia. The sources of ammonia are soil, ocean, and pollution from cities. Humus is often present in rain water, and Dhar and Ram (1933) report a content of 0.00015–0.0012 g/l formaldehyde, $\text{H} \cdot \text{CHO}$, as a constituent of precipitation.

The gases dissolved in rain water consist of approximately 63 per cent nitrogen by volume, 34 per cent oxygen, and 3 per cent carbon dioxide and other gases. Oxygen and carbon dioxide are definitely enriched in these gases, as compared with their concentration in the air, and thereby the reaction rate of rain water is increased.

TABLE 7.3
INORGANIC CONSTITUENTS IN RAIN WATER

COMPOUND	CONCENTRATION IN RAIN (mg/kg)	
	City of Knoxville, Tennessee, U S.A.	1½ Miles from Center of Knoxville
K	5 5	2 6
Na	3 6	1 5
Ca	2 8	0 9
Mg	0 7	0.4
SO ₄	14 5	5 6
Cl	6 5	3.3

The chemical composition of rain water is highly variable, depending on the proximity of the sea, the character of the surrounding country, density of population, and the industrial activities of man. The smoke from cities and industrial districts may cause an increase of several hundred per cent in the SO_3 and CO_2 content of rain water over the amounts found in rural districts. On the other hand, the content of chlorine and nitrogen does not vary widely in such cases (Riffenburg, 1925). Changes in the composition of rain water which depend on the surroundings are illustrated by the analyses in Table 7.3, carried out by MacIntire and Young (1923) and recalculated by Conway (1942). The values recorded show that the content of the inorganic constituents decreases rapidly on passing from the center of contamination.

During rainfall the composition of the precipitation varies. The purest water is obtained from rain after tropical thunderstorms. High winds cause the presence of much dust in the atmosphere, which increases the content of dissolved solids in rain water.

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It is evident that no good average composition can be calculated for the precipitation, although some authors have preferred to use averages calculated from a large number of individual rain-water analyses. However, many of the old analyses seem to be unreliable (cf. Bertrand, 1935; Volk, Tidmore, and Meadows, 1945). Comparatively little reliable information is consequently available on the composition of the different forms of precipitation.

Some analyses of rain water are collected in Table 7.4, according to Riffenburg (1925), Shutt and Hedley (1925), and Israël (1934). This

TABLE 7.4
COMPOSITION OF RAIN WATER

CONSTITUENT	AVERAGE RAIN WATER (RIFFEN- BURG)	RAIN WATER, WASHING- TON, D C, U.S.A. (RIFFEN- BURG)	RAIN AND SNOW, CANADA (SHUTT AND HEDLEY)	RAIN, LEIDEN, NETHER- LANDS (ISRAEL)	RAIN, MOUNT VERNON, IOWA, U.S.A.	SNOW, MOUNT VERNON, IOWA, U.S.A.
	Parts per Million (g/ton)					
Chlorides.....	3 0	trace-3 0		4 18	0-46.15	0-120 7
Sulfates....	5 0	1 0-17 0			0-283 40	0-14
Nitrates.....	0 2		} 0 278		0-6.000	0-2 3
Nitrites. . . .					0-1.35	0-1 00
Free ammonia .	0 4		0 515		0-14 20	0-1 6000
Albuminoid am- monia			0 114		0-28 00	0 002-2.200
pH.....		4 4-7 7				

table also contains the ranges in concentration obtained at Mount Vernon, Iowa, U.S.A., until 1938, according to analyses published by numerous authors.¹

Chlorides are among the most abundant constituents of precipitation, and, along with carbon dioxide and sulfates, they are geochemically the most important constituents therein. The average chloride content of rain falling on continental areas would seem to be 3-4 g/ton, but Collins and Williams (1933) suggest, on the basis of more than two hundred analyses of rain water collected in the United States, that the content of chloride is less than 0.3 g/ton. The higher values are due to contamination by the soot and fumes resulting from the combustion of fuel in cities and by the spray near the seashore

1. These analyses are published in numerous papers in the *Monthly Weather Review*.

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when the wind is landward. In the latter case the chloride content may be very high. Irwin (1925) reports as much as 226 g/ton NaCl in rain water when the sea has had a few days of storm, and Miller's (1914) maximum chlorine content is 3,920.0 g/ton in rain water collected at Butt of Lewis, Outer Hebrides, Scotland. A fall of salt crystals was reported in Mantua, Italy, in 1879. Jacobs' (1937) analyses prove that there is considerable chloride in the air and that the supply is continually being replenished from the sea. The sea-water droplets suspended in the air are semipermanent constituents, being able to remain therein until removed through condensation and precipitation. The chloride content of air near the sea is, according to Jacobs, $0.076\text{--}0.518\text{ mg}\cdot\text{m}^{-3}$, corresponding to 0.125 and $0.854\text{ mg}\cdot\text{m}^{-3}$ NaCl, respectively. Free hydrochloric acid as a constituent of rain water is of only local importance near centers of volcanic activity.

The sulfate content of rain water is highly variable. The normal maximum content in precipitation is 2 g/ton (Collins and Williams, 1933). Most of the sulfate in rain water comes from hydrogen sulfide, generated in shallow water on the continental shelves (Conway, 1942), but the combustion of bituminous coal used for heating and industrial purposes seems to be an important local source. The SO_2 produced oxidizes in the air rapidly to SO_3 . Additional sulfate is sometimes furnished by dust storms. The SO_3 content of rain water near cities and industrial districts is higher during the winter than in summer, owing to the greater amount of fuel consumed. MacIntire and Young (1923) believe that the major portion of sulfate in precipitation derives from solid matter rather than from dissolved gases.

Several comparative studies show the great differences in the sulfate content of rain water from rural districts and from industrialized areas. Schulz (1930) found $1.5\text{--}33.2\text{ g/ton SO}_3$ in rain water and snow at a distance of $7\frac{1}{2}$ km from Hamburg, Germany, and $13.9\text{--}45.5\text{ g/ton}$ in precipitation falling in the harbor of the same city. Some of the analyses of MacIntire and Young (1923) are given in Table 7.3. They found that the sulfur content in the rain ran parallel with the consumption of soft coal. Very high values were obtained near sulfide-ore smelters. According to Volk, Tidmore, and Meadows (1945), the amount of SO_3 per unit of surface in an industrial district in Alabama in the United States was 4.9–10.6 times as great as the average for rural districts.

The nitrogen compounds in rain and snow have been investigated

extensively because of their agricultural value as soil fertilizers. The averages given by Riffenburg (1925) and by Shutt and Hedley (1925) are presented in Table 7.4. High nitrogen corresponds to high precipitation; snow is decidedly lower in nitrogen compounds than is rain. The differences in the nitrogen figures are due to changes in the biochemical activity in the soil. After high winds the content of free and albuminoid ammonia in rain water increases, owing to the presence of much dust in the atmosphere. Miller (1914) found that nitrogen is largely present as ammonia in most inland rains, whereas in places near the sea, especially in tropical countries, nitrates tend to preponderate. This is due to the increased production of nitrates in the atmosphere in coastal rains because of violent thunderstorms. The content of ammonia nitrogen in rain water is lower near the seashore than in inland areas. The biochemical processes taking place in the soil are the chief source of ammonia nitrogen in rain water.

The amount of carbonate and bicarbonate in average rain water is low (Conway, 1942). Phosphates are uncommon. The content of iron and aluminum in precipitation is normally negligible.

Lime and magnesia are often present in considerable quantities in rain water. They are partly derived from small particles of limestone dust and silicates found in the air as a result of combustion, industrial use of limestone, and uptake of carbonate- and sulfate-bearing dust by wind. Bertrand (1946), studying the Mg:Ca ratio in rain water and in outcropping calcareous rocks and industrial products derived therefrom in the area investigated, found much more magnesium in relation to calcium in rain water, in analogy with the relationships of these metals in sea water. Since the Mg:Ca ratio of sea water is hundreds of times as high as that of limestones, the magnesium present in rain water is easily explained as deriving from the sea.

If air lies in contact with a given part of the hydrosphere, it may, under certain circumstances, become saturated with water vapor. This results in the condensation of the water and in the formation of fog, mist, dew, rime, and the various forms of precipitation. Köhler (1925) established the presence of calcium and magnesium in rime and found that the Mg:Cl ratio therein corresponds to that in ocean water. He (Köhler, 1937) gives the averages based on analyses made at the Haldde Observatory in northern Norway shown in Table 7.5. The values show that the chlorine content of the precipitation is high enough to be responsible for all chlorine found in the surface water.

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Houghton's (1948) analyses of fog and cloud water are given in Table 7.6. His analyses also show the predominance of chlorides and sulfates near the seashore in these forms of atmospheric water. The pH values are a measure of the bicarbonate content (Conway, 1942) and show a higher concentration of this anion in the inland cloud water.

TABLE 7.5
CHLORINE CONTENT OF PRECIPITATION AND SURFACE
WATER AT THE HALDDE OBSERVATORY, NORWAY

Water Derived from—	Average Content of Cl (mg/l)
Rain (Israel, 1934)	3 42
Snow	2 097
Lakes and creeks	1.058–2 744

TABLE 7.6
AVERAGE CONTENT OF DISSOLVED SUBSTANCES IN FOG AND CLOUD WATER

COMPOUND	FOG, KENT ISLAND, NOVA SCOTIA, CANADA	FOG, COAST OF MAINE, U.S.A.	FOG, SE. COAST OF MASSACHU- SETTS, U.S.A.	CLOUD, MOUNT WASHINGTON, NEW HAMPSHIRE, U.S.A.
	Parts per Million			
Chlorides	7 5		35	0.1
Sulfates	13	28	18	7
pH	7 0			4 5

CYCLE OF WATER AND SUBSTANCES DISSOLVED THEREIN IN THE ATMOSPHERE

The atmosphere forms an important stage in the constant cycle of water and the substances dissolved therein. Wüst (1936) has presented values for the water economy of the Earth, as being the most probable ones, which are reproduced in Table 7.7. The values show that $334 \cdot 10^3$ km³ water is evaporated from the oceans yearly. Of this, $297 \cdot 10^3$ km³ returns directly to the sea, whereas the rest, $37 \cdot 10^3$ km³, is supplied by runoff. On the land the difference between the annual rainfall and the water supplied by evaporation from inland basins and from soil is $37 \cdot 10^3$ km³, which is produced by evaporation of ocean water.

The surface of the ocean is constantly agitated by wind and waves, and consequently much water is temporarily suspended in the at-

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mosphere in the form of spray or small droplets of concentrated sea water. The water in the droplets evaporates and leaves the salts soaring in the air as small particles. According to Jacobs (1937), the number of the salt particles everywhere in the atmosphere is of the same order because the surface of the ocean is five-sevenths of the total surface area of the Earth, and the addition of salt particles and the mixing in the atmosphere are continuous processes. Many of the salt particles are of small size, thus being able to remain suspended in the air semipermanently and to travel long distances. They are finally brought down in precipitation and ultimately reach the sea, whereby their cycle is completed (cyclic salts). In 1877 Franz Pošepný, the Hungarian geologist, attributed the presence of sodium chloride in inland waters largely to cyclic salts. Quantitative calculations,

TABLE 7.7
ANNUAL PRECIPITATION AND EVAPORATION
ON THE EARTH

Area	Precipitation (10^3 km^3)	Evaporation, (10^3 km^3)
Ocean	297	334
Land	99	62
Total.	396	396

showing the amount of these salts in river water, were published by Conway (1942; see chap. 6).

The salt particles are believed to be important as condensation nuclei (Köhler, e.g., 1941; Israël, 1934; Jacobs, 1937). Other nuclei consist of small hygroscopic particles of dust and combustion products, aggregates of gas molecules, some liquid particles, e.g., small droplets of sulfuric acid in industrial areas, etc. The oceans contribute most of the nuclei over and near them, whereas the nuclei resulting from combustion are important near their sources. The salt content of precipitation, as compared with that of sea water, is presented in Table 7.8, which is quoted from Jacobs (1937), who uses Köhler's rain-water analyses.

The percentages of sodium chloride and magnesium chloride in the rain and in sea water are almost identical, and this fact affords proof of the marine origin of the dissolved salts.

The analyses of precipitation given in the preceding paragraphs show that the content of dissolved salts is greatest near the seashore

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and falls off with growing distance from the sea, because only a part of the suspended salts is carried inland by the winds. Köhler (1925) calculated that the amount of salts carried annually from the sea to

TABLE 7.8
DISSOLVED SALTS IN SEA WATER AND IN PRECIPITATION

SALT	SEA WATER		PRECIPITATION	
	Concentration in Parts per Thousand	Per Cent of Total	Concentration in Parts per Million	Per Cent of Total
NaCl	27.213	77.758	5.03	77.50
MgCl ₂	3.807	10.875	0.70	10.79
MgSO ₄	1.658	4.737	0.47	7.24
CaSO ₄	1.260	3.600	0.29	4.47
K ₂ SO ₄	0.863	2.465		
CaCO ₃	0.123	0.345		
MgBr ₂	0.076	0.217		
Total	35.000	99.997	6.49	100.00

TABLE 7.9
YIELD OF SALTS CONTAINED IN PRECIPITATION
IN NORMANDY, FRANCE, IN 1851

Compound	kg/hectare
NaCl	37.5
KCl	8.2
MgCl ₂	2.5
CaCl ₂	1.8
Na ₂ SO ₄	8.4
K ₂ SO ₄	8.0
CaSO ₄	6.2
MgSO ₄	5.9
Na	17.4
K	7.9
Ca	2.4
Mg	1.9
Cl	29.5
S	6.4

the atmosphere is $196,985 \cdot 10^4$ tons. This amount is already of a certain geochemical moment. According to the old analyses of Pierre, quoted by Clarke (1924), the annual yield of salts per hectare in Normandy, France, in 1851 was as shown in Table 7.9. However, MacIntire and Young (1923) conclude that the bulk composition of soil is not more changed by rainfall than it would be if the precipitation consisted of pure water.

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THE BIOSPHERE AS A GEOCHEMICAL SPHERE

THE biosphere consists of plants, animals, and micro-organisms. The concept of the biosphere was introduced into biology early in the nineteenth century by the French naturalist, Jean de Lamarck (1744–1829). The importance of the vegetable and animal organisms in geological phenomena was emphasized, in 1875, by the Austrian geologist, Eduard Suess (1831–1914), who also introduced the name biosphere to denote organic Nature as a whole. The biosphere occupies the lower part of the troposphere, probably the whole hydrosphere, and forms, in addition, a thin layer on the lithosphere. It is the region where changes caused by the radiation of the Sun take place. It is the part of the Earth which is capable of sustaining life. Contrary to the hydrosphere, the biosphere is more uniformly distributed over the total surface of the Earth, and only in polar regions, on top of the highest mountains, and in deserts is biological activity slight or negligible.

The upper limit of the biosphere lies at a height of approximately 5 km in the troposphere. Spores have been found at a height exceeding 4,800 m, and Glick (1939) has collected insects and spiders at 4,200–4,500 m. The lower limit of the biosphere lies at a depth of 1,800 m in the lithosphere, where ZoBell (1946a) found living bacteria in oil-well brines. Bacteria are present on the ocean bottom, at a depth in excess of 4,800 m.

The biosphere is usually divided into three main parts or habitats, called biocycles—the terrestrial, fresh-water, and marine biocycles. The latter is, quantitatively, the most important of the three. It affords approximately three hundred times as much inhabitable space for plants and animals as do the two other biocycles together. The importance of the marine biocycle is illustrated by the fact that most

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of the Earth's oxygen is produced therein, as is also the bulk of organic substances synthesized. According to Riley (1944), the total oceanic carbon metabolism is around $126 \cdot 10^9$ tons per year and the total for the entire Earth about $146 \cdot 10^9$ tons.

The marine biocycle consists of the benthic and pelagic divisions. The former includes the ocean floor, whereas the latter consists of the total mass of sea water. Marine organisms play an important role in the cycle of the inorganic and organic substances in the sea. Sea water is an ideal environment for living cells because it contains all the elements essential for the growth and maintenance of cytoplasm.

The fresh-water biocycle forms a small fraction of the terrestrial biocycle. The atmosphere is not considered to form a biocycle because permanent life does not exist therein. However, the atmosphere as a transitory abode of life is of some geochemical interest. Bacteria are often abundant in air masses of continental origin. Spores and pollen are reported to soar as high as approximately 5 km in the air. Insect particles in the atmosphere may be more abundant than all the pollen, and the total number of insects in an air column with a base of 1 square mile between 15 and 4,200 m over the Earth's surface averages 25,000,000 (Glick, 1942).

The branch of geochemistry dealing with the biosphere is often called biogeochemistry. The importance of organisms as geological agents was emphasized by F. W. Clarke in the various editions of his *Data of Geochemistry*. The effect of the biosphere on chemical phenomena taking place on the surface of the Earth has been extensively studied, since 1916, by V. I. Vernadsky, followed by A. P. Vinogradov and other scientists at the Biogeochemical Laboratory of the Academy of Sciences of the U.S.S.R., founded in 1929.

If the weight of the biosphere is taken as unity, the relative weights of the three uppermost geochemical spheres of the Earth may be expressed by the following figures:

Hydrosphere.....	69,100
Atmosphere.....	300
Biosphere	1

The relative weight of the uppermost part of the lithosphere, using the same unit, would be of the order of 10^6 . In spite of the negligible mass of the biosphere, as compared with the other geospheres, its chemical activity is remarkable and its geochemical effect important. Thus the number of the plant and animal species constituting the biosphere is very high, as compared with that of the mineral species.

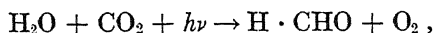
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About 2,000 minerals are now known, whereas, so far, nearly 200,000 different plants and 800,000 animals are found to exist in the biosphere. Most, if not all, of the free oxygen in the atmosphere is considered to be the result of the chemical activity of the biosphere (photosynthesis). The chalk cliffs and coral reefs afford proof of profuse biochemical activity, and the floor of the ocean is covered by millions of square kilometers of siliceous sediments, produced by marine organisms, starting with a silicon content of 0.02–4.0 g/ton in sea water. All carbon deposited in organogenic sediments was originally collected from the atmosphere containing about 0.03 per cent carbon dioxide by volume. These and other examples show that, in spite of its small mass, the biosphere is geochemically as important as the other geospheres. It should be noted, in addition, that the biosphere is an important agent in the migration and concentration of many elements forming ore deposits, some of which are of high economic importance.

The green chlorophyll-containing plants in the biosphere are able to synthesize organic compounds from inorganic substances. The main raw materials for this process are carbon dioxide and water, which are united in photosynthesis. The opposite process is the respiration by which the organic carbon compounds synthesized by plants are oxidized. Respiration is the main source of the energy needed in the functions of animals.

The activity of plants, animals, and micro-organisms in the biosphere results in the formation of a number of sediments, such as coal, brown coal, and petroleum; organogenic carbonate and siliceous sediments; phosphorite; and guano. However, these sediments are not usually considered a part of the biosphere proper.

The biosphere is the youngest of the geochemical shells of the Earth. The oldest trace of organic activity so far encountered is the Archean fossil, *Corycium enigmaticum* Sederholm (Rankama, 1948a), possibly a primitive alga, whose age is about 1,400 million years. The formation of the biosphere may have been started by the photochemical formation of simple organic compounds (Wildt, 1943). The photochemical synthesis of formaldehyde,



is believed by many scientists to be the first step in the generation of life on the Earth.

BIOPHILE CHARACTER OF THE ELEMENTS

The classification of the elements according to their geochemical nature given in Table 4.3 reveals the presence of a group of biophile elements. These are elements occurring typically in the biosphere. Apart from the biophile elements proper, all those known to be present in organisms are called biological elements. They are known to vary considerably in importance, amount, and distribution in the organisms. Some of them are basic elements met in every organism, whereas others occur only in certain species. Among the basic elements, oxygen is essential for the maintenance of animal life, nitrogen and carbon for that of the plants, and hydrogen and oxygen (as water) for all living organisms. So far, sixty elements have been found to be present in the biosphere. Combined, they form all biological material, which is composed chiefly of water, carbohydrates, proteins, and lipids. These compounds participate in chemical reactions with their environment.

Fearon (1933, 1947) has classified the biological elements according to their content in the organisms (Table 8.1). Radium is added to Table 8.1 because it is concentrated by some organisms. There are eighteen invariable elements, among which the primary ones make up the bulk of all living matter; they are found in all known organisms and largely determine their physical structure. The invariable secondary elements, even though equally indispensable, are present in much lower percentages, and the content of the invariable microconstituents is minute. Among the variable elements, some are found in relatively high concentrations in certain species, whereas they are absent in other, even related, species. Notable differences are also found between plants and animals with reference to their composition. To use the metaphor of Bertrand (1939), the plants and animals, from a chemical viewpoint, appear as a certain kind of oligarchy, in which an immense crowd, consisting of atoms of indispensable framework-forming elements, is governed by a minority of catalysts.

The biological elements have a number of important functions in the organisms (Fearon, 1947). Carbon and nitrogen are found in the framework of plant and animal tissue. Calcium, magnesium, fluorine, silicon, and phosphorus occur in the hard shells and skeletons of many organisms. Hydrogen and oxygen are energy-exchange elements. Some elements are found as electrolytes and osmotic regulators in cell liquors (Na, K, Ca, Mg, Cl as chloride, C as carbonate,

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and P as phosphate). Still others act as catalysts in oxidation-reduction systems (Fe, Cu, Mn, Zn, I, S), or as activators of enzymes (Ca, Mg, Co). Certain elements may replace others in their functions (Be substitutes for Ca and Mg; Sr and Ba for Ca). The function of some elements, e.g., nickel, molybdenum, and silver, is still very incompletely known.

The presence or absence of an element in an organism depends primarily on its physiologic functions. Some elements are present only

TABLE 8.1
DISTRIBUTION OF ELEMENTS IN ORGANISMS AS PER-
CENTAGE OF BODY WEIGHT

INVARIABLE			VARIABLE		
Primary 60-1	Secondary 1-0.05	Microconstitu- ents <0.05	Secondary	Microconstitu- ents	Contaminants, among Others
H C N O P	Na Mg S Cl K Ca Fe	B F Si Mn Cu I	Ti V Zn Br	Li Be Al Cr Co Ni Ge As Rb Sr Mo Ag Cd Sn Cs Ba Pb Ra	He A Se Au Hg Bi Tl

as temporary constituents; others are essential for the normal evolution and functions of the organism, and in some cases their detailed role in the metabolic processes is known. An element may be considered essential if its absence causes functional disturbances in the organism; but this does not imply that it is necessarily essential for any other organism because the requirements of even closely related species may be different. Some elements may be accumulated by organisms far beyond all physiologic requirements, if any. Some non-essential elements may be concentrated in plants as a result of their defective power of selection. The plants often cannot distinguish between essential and nonessential elements, especially because the

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final evaluation of the elements seems to take place within the plants in the cytoplasm of the cells. The nonessential elements taken up by plants act only as fellow-travelers of the essential ones.

The role of the various elements in biogeochemical processes will be discussed in Part II of this book.

POSITION OF THE BIOLOGICAL ELEMENTS IN THE PERIODIC TABLE

Several attempts have been made to establish the relationships between biophile elements and the Periodic Table. Thatcher (1934) pointed out that nearly all elements having a function in plant nutrition are found in the first four periods of the Periodic System, whereas the heavier elements, with the exception of molybdenum, are not necessary for plants. Another relation between the elements essential for plants and the Periodic System was established by Frey-Wyssling (1935) on the basis of earlier results which indicated that potassium, chlorine, and calcium, because of their atomic structure, are the least toxic elements to plants. When a line is drawn in the Periodic Table to connect carbon and argon, it passes through, or near, the places of all the essential elements. The line is called the nutrient line. It is shown in Figure 8.1, modified from Frey-Wyssling (1935).

The general relationship between the biological elements and the Periodic System is shown in Figure 8.2, which is adapted from Webb and Fearon (1937). According to these authors, the invariable biological elements, with the exception of lithium and beryllium, occur above the upper (dashed) line. Variable elements are those between the two lines, and the contaminants and nonbiological elements occupy places below the continuous line. Leuthardt (1941) has explained this regularity as a result of the assumption that the capacity of plants to collect elements of a group or subgroup in the Periodic System changes continually with the atomic weight. Consequently, if the plant cannot distinguish between the n th and the $(n + 2)$ th element within a group in this respect, its selection power does not suffice to distinguish between the n th and the $(n + 1)$ th element either, and the result is a gapless arrangement of the elements.

THE AVERAGE CHEMICAL COMPOSITION OF LIVING MATTER

Single species of plants and animals, although of high importance in biology and partly also in biochemistry, are of minor importance in biogeochemistry proper. The average chemical composition of all

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animal and vegetable matter, on the other hand, is of high importance for the geochemical knowledge of the biosphere. It must be stated, however, that the information available on this subject is very scarce.

1		(H)											He	
2	He	Li	Be	(B)	(C)	(N)	(O)	F				Ne		
3	Ne	Na	(Mg)	(Al)	(Si)	(P)	(S)	(Cl)				A		
4	A	(K)	(Ca)	Sc	Ti	V	Cr	(Mn)	(Fe)				Co	Ni
		Cu	(Zn)	(Ga)	Ge	As	Se	Br	Kr					
5	Kr	Rb	Sr	Y	Zr	Cb	(Mo)	Tc	Ru				Rh	Pd
		Ag	Cd	In	Sn	Sb	Te	I	Xe					
6	Xe	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os				Ir	Pt
		Au	Hg	Tl	Pb	Bi	Po	At	Rn					
7	Rn	Fa	Ra	Ac-Cm										

1 (C) 2 Cu 3 (Cl)

FIG. 8.1—The biological elements in the Periodic Table and the nutrient line. 1, basic elements; 2, other essential elements; 3, elements enriched by certain organisms.

1			H								He		
2	He	Li	Be	B	C	N	O	F	Ne				
3	Ne	Na	Mg	Al	Si	P	S	Cl	Ar				
4	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe		Co	Ni	
		Cu	Zn	Ga	Ge	As	Se	Br	Kr				
5	Kr	Rb	Sr	Y	Zr	Cb	Mo	Tc	Ru		Rh	Pd	
		Ag	Cd	In	Sn	Sb	Te	I	Xe				
6	Xe	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os		Ir	Pt	
		Au	Hg	Tl	Pb	Bi	Po	At	Rn				
7	Rn	Fa	Ra	Ac-Cm									

FIG. 8.2—The three groups of the biological elements in the Periodic Table

In Table 8.1 a classification of the biological elements was presented according to their importance and content in the organisms. Vinogradov (1933) states that the chemical composition of all organisms is very similar, if such elements as carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur are considered, whereas the content of the trace constituents of the organisms shows great variations from species to species.

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In general, the average chemical composition of the organisms is reminiscent of the composition of their environment. It appears to be probable that the quantitative chemical composition of an organism is a specific feature. However, there are relatively constant ratios between carbon, nitrogen, and phosphorus in all living matter. With special reference to animals, the elementary composition of vertebrates appears to be more constant than that of invertebrates. In the former the trace elements, even when essential, are found in very minute quantities as compared with their amounts in some lower organisms (Webb, 1937).

TABLE 8.2
AVERAGE CHEMICAL COMPOSITION
OF ORGANIC MATTER*

ELEMENT	PERCENTAGE COMPOSITION OF—		
	Carbohydrates	Fats	Proteins
O	49 38	17 90	22 4
C	44 44	69 05	51 3
H	6.18	10 00	6 9
P		2 13	0 7
N		0 61	17 8
S		0 31	0 8
Fe			0 1
Total	100 00	100 00	100 0

* Based on material from *Textbook of Comparative Physiology*, by C. G. Rogers. Copyright 1938. Courtesy of McGraw-Hill Book Co.

The primary invariable elements are essential constituents of carbohydrates, lipids (fats), and proteins. Some other invariable elements are also always present in the two last-mentioned groups of compounds.

The following principal groups of substances can be established in the organisms: (1) organic material, largely carbohydrates, lipids, and proteins; (2) inorganic skeletal structures; (3) inorganic compounds dissolved in body fluids. The average composition of organic material is presented in Table 8.2, according to Rogers (1938).

The skeletal material consists mainly of calcium carbonate, calcium phosphate, or silica. Analyses of skeletal material of some marine organisms are presented in Table 8.3, the values recorded being quoted from those published by Clarke and Wheeler (1922). Sometimes magnesium carbonate occurs as an important constituent of calcareous shells. It should be noted that sodium and chlorine, al-

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though the most abundant elements of sea water, are not present in skeletal material. This is due to the high solubility of their compounds.

Bertrand (1939) has published two analyses, showing the average total composition of man and the fabaceous forage plant, alfalfa. These analyses are given in Table 8.4. The values reproduced show that living matter consists nearly exclusively of eleven elements. As to the trace elements, iron is the most abundant one in man (0.005 per cent, dry weight). Zinc comes next, with a content of 0.002 per cent, followed by copper (0.0004 per cent) and manganese (0.00005

TABLE 8.3
REDUCED ANALYSES OF SKELETAL MATERIAL OF SOME MARINE ORGANISMS

COMPOUND	FORAMINIFER (<i>Orbulina adunca</i>)	CALCAREOUS ALGA (<i>Lithothamnium erubescens</i>)	PHOSPHATIC BRACHIOPOD (<i>Discinisca lamellosa</i>)	STONY CORAL (<i>Mussa</i> aff. <i>M. dipsacea</i>)
	Per Cent by Weight			
SiO ₂	0.11	0.20	0.85	0.15
(Al,Fe) ₂ O ₃	0.09	0.13	0.58	0.05
MgCO ₃	10.04	16.96	6.68	0.09
CaCO ₃	89.76	81.59	8.35	99.71
CaSO ₄		1.12	8.37	(?)
Ca ₃ P ₂ O ₈	trace	trace	75.17	trace
Total	100.00	100.00	100.00	100.00

per cent). The concentration of the constituents varies in different plants and animals. It should be noted that sodium and calcium are usually trace constituents in plants and that in many animals (vertebrates) calcium is a primary constituent. Compared with animals, plants are usually richer in manganese, nickel, aluminum, titanium, and boron but are impoverished in iron, zinc, and copper.

In general, elements of low atomic number predominate in the organisms. Such elements are enriched therein and form compounds that migrate readily, such as gases, soluble salts, etc., whereas other elements are impoverished which do not have this property, e.g., titanium, zirconium, and thorium; they form salts which are easily hydrolyzed.

With reference to the single elements in nondehydrated organisms, the content of oxygen is more than 50 per cent of the mass of both plants and animals. Hydrogen comes next, with an average content

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of more than 10 per cent. The third place is occupied by carbon, the element most typical of organic Nature. The carbon content varies between a maximum of 10–20 per cent in some terrestrial plants and animals and a minimum of less than 0.1 per cent in many organisms living in water. The plants form the bulk of the biosphere, and their carbon content is, according to Noddack (1937), approximately sixty times as high as that of animals.

The average compositions presented in Table 8.4 show clearly that many of the constituents of the organisms are decisively impover-

TABLE 8.4
AVERAGE TOTAL COMPOSITION OF LIVING MATTER

ELEMENT	ADULT MAN (<i>Homo sapiens</i>)	ALFALFA (<i>Medicago sativa</i>)
	Per Cent of Dry Weight	
C	48 43	45 37
O	23 70	41 04
N	12.85	3 30
H	6.60	5.54
Ca	3.45	2 31
S	1.60	0 44
P	1.58	0 28
Na	0 65	0 16
K	0 55	0 91
Cl	0 45	0 28
Mg	0 10	0 33
Total	99 96	99 96

ished with reference to their concentration in the Earth's crust (see Table 2.3). This phenomenon is most pronounced in the case of silicon, aluminum, and iron and is well discernible for sodium, potassium, and magnesium. The most important invariable elements, like carbon, hydrogen, nitrogen, phosphorus, chlorine, and sulfur, on the other hand, are concentrated in living matter. The oxygen and calcium content is of a similar degree of magnitude in both cases. Hutchinson (1945) has presented a diagram showing the ratio of the mean concentration of elements in living plants to that in the upper lithosphere. This diagram, reproduced in Figure 8.3, shows the importance of the above ratio in determining the biological availability of the elements.

If the average contents presented in Tables 8.1 and 8.4 are compared with those showing the abundance of the elements in the upper

lithosphere (Table 2.3), it becomes evident that the organisms are able to select the necessary biological elements irrespective of their concentration in the environment, which is ultimately the Earth's crust. Similarly, a comparison of the two tables with Table 6.17 gives the same result with reference to sea water. On the other hand, it must be noticed that some of the more abundant elements of the uppermost lithosphere are used by organisms only with reluctance or will not be taken up at all.

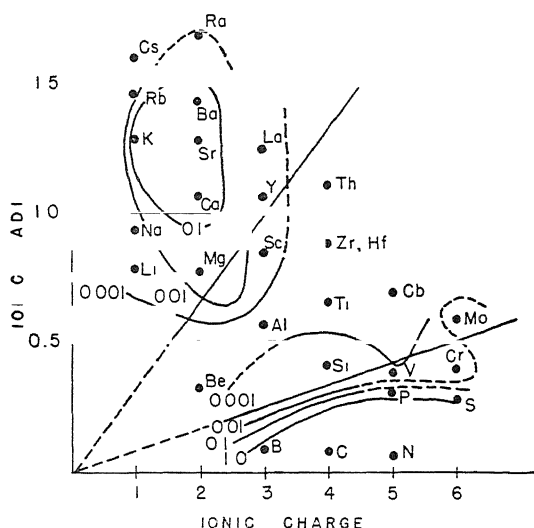


FIG. 8.3.—Concentration ratio of elements in living plants and in the upper lithosphere. (Based on material from *Soil Science*, Vol. 60, 1945. Courtesy of The Williams & Wilkins Company).

ESSENTIAL ELEMENTS IN PLANTS AND ANIMALS

The organic life has deeper roots in inorganic substances than was previously believed. According to classical plant physiology, the following ten elements are essential for the healthy growth of plants: C, H, O, N, S, P, K, Ca, Mg, and Fe. The seven last-mentioned elements in this group are called the major nutrients or the mineral nutrients. The electrically positive elements among these are taken up by plants as positive ions, whereas the electrically negative ones are introduced in the form of complex ions: nitrates (or ammonium), carbonates, phosphates, and sulfates. Oxygen is brought in as free molecules, as complex anions, and as water. Hydrogen is carried as the H^+ ion or as undissociated water, and carbon in the form of products formed in photosynthesis and as water-soluble carbonates.

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However, later studies have revealed that these ten elements alone do not suffice to guarantee the growth and life of plants. Many other elements are now known to be essential for plants or to promote their growth. Thus boron, manganese, copper, zinc, molybdenum, and perhaps gallium are essential for the healthy growth of plants. These elements are called the micronutrient elements, because their characteristic physiological effects are combined with administration in small amounts. Some elements are, by laboratory experiments, found to promote, if present in small amounts, the growth of some plants. This group includes, among others, lithium, titanium, tin, vanadium, fluorine, bromine, iodine, and nickel. In greater concentrations nearly all these elements are highly poisonous. Still other elements are believed to have a role in plant nutrition, but they have, so far, not been studied in detail. Some elements, like aluminum, silicon, and chlorine, are known to be accumulated at least in some species or genera, and it is possible that they are, in small quantities, essential for such plants. However, it cannot be concluded that an element which stimulates growth is necessarily essential for growth. The absolute amount of a trace element is often not of decisive importance, whereas the relative amounts of two or more may be most significant. Certain elements—manganese, zinc, aluminum, magnesium, and iron—which form an essential part of the structure of vitamins and enzymes in particular, are directly associated with vital life-processes where these substances are involved.

Most of the essential and micronutrient elements occupy places in the neighborhood of the nutrient line. With the exception of hydrogen, the rule is valid which states that the toxicity of an element increases with greater distance from the nutrient line. Thus, for instance, in the series K-Rb-Cs, Ca-Sr-Ba, and Zn-Cd-Hg, the first element is indispensable, whereas the last one is toxic. This fact shows that toxicity, in general, increases with increasing atomic number when elements belonging to the same group or subgroup are considered. However, on the right-hand side of the Periodic Chart there are exceptions to this rule: arsenic seems to be more poisonous than antimony or bismuth, and tungsten is less toxic than chromium. The toxic effects depend, in addition, rather remarkably on the individual properties of the plant species.

The well-established indispensable elements in animals are C, H, O, N, S, P, Na, K, Mg, Ca, Fe, and Cl. In addition, the following trace elements are known to be essential: I, Mn, Cu, Zn, and Co. Al-

though cobalt probably has no role in plant nutrition, it is known to be essential for ruminant animals, which collect their supply from plants. Many other trace elements are also established as constituents of animals; but, compared with the knowledge concerning the occurrence and role of minor elements in plants, the information available on animals is still far from exhaustive.

It is interesting to note the high biological importance of magnesium and iron, which are essential constituents of chlorophyll and hemoglobin, respectively. Without the two metals these compounds would not exist at all.

PLANTS AND ANIMALS AS ACCUMULATORS OF ELEMENTS

Certain organisms are accumulators of definite elements. Some plants are found to tolerate large quantities of elements which, even in small doses, are strong poisons to other species. Plants also accumulate and concentrate certain elements in their cells, especially in the green parts. Thus, e.g., aluminum is concentrated in many plants of the family Lycopodiaceae; silicon accumulates in monocotyledons; sodium and chlorine in halophytes. Some seashore plants concentrate rubidium from sea water, and radium accumulates in the genus *Lemna* in the spring and returns to sea water in the autumn upon the death of the plant. These elements are not essential for the species in question, and the concentration is totally independent of their value as plant nutrients. They are called ballast elements (*Ballaststoffe*; Frey-Wyssling, 1935). Even in the case of essential elements the most part of the supply in the plant organism is inactive, being stored away in cells as a reserve.

Goldschmidt (1930*b*) established the remarkable concentration of germanium in coal ashes; and continued studies by Goldschmidt and Peters (1933*c*) revealed the fact that many coal and brown-coal ashes contain exceptionally high amounts of certain trace elements as compared with their average content in the Earth's crust. Examples of the accumulation are shown in Table 8.5, which is based on values reported by Goldschmidt (1937*a*). A high degree of enrichment can be expected only in coals with a low ash content, and the following elements are concentrated in coal ashes: Li, Be, Sr, Ba, B, Sc, Y, rare-earth metals, Zr, Hf, V, Co, Ni, Mo, Rh, Pd, Pt, Cu, Zn, Ga, Ge, As, (Se²), Ag, Cd, In, Sn, Sb, I, Au, Tl, Pb, and Bi. Some coal ashes may also be exceptionally high in manganese. Stutzer (1940) quotes as high a content as 2.84 per cent MnO. Some coal ashes from

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New Zealand may contain up to 48,000 g/ton boron (Coal Survey Committee, 1943), but such phenomenal percentages are probably attributable to the action of adjacent thermal waters. The above list contains elements belonging to the most diverse groups of the Periodic System. Along with typically lithophile elements, like beryllium, zirconium, and the rare-earth metals, noble metals with a pronouncedly siderophile character are enriched in the coal ashes. Chalcophile

TABLE 8.5
ACCUMULATION OF ELEMENTS IN COAL ASHES

ELEMENT	CONTENT IN COAL ASHES (g/ton)		CONTENT IN IGNEOUS ROCKS (g/ton)	ENRICHMENT FACTOR	
	Maximum	Average		Maximum	Average
Li	500		65	8	
Be	1,000	300	6	170	50
B	3,000	600	3	1,000	200
Sc	400	60	5	80	12
Co	1,500	300	23	65	13
Ni	8,000	700	80	100	9
Zn	10,000	200	132	76	1.5
Ga	400	100	15	27	7
Ge	11,000	500	7	1,600	70
As	8,000	500	5	1,600	100
Y	800	100	23 1	28	4
Zr	5,000		220	23	
Mo	500	200	2.5-15	200-33	80-13
Ag	5-10	2	0.10	100-50	20
Cd	50	5	0.15	333	33
In	2		0 1	20	
Sn	500	200	40	13	5
Pt	0 7		0 005	140	
Au	0.2-0 5		0 005	100-40	
Tl	5	1	0 3-3	17-2	3-0 3
Pb	1,000	100	16	63	6
Bi	200	20	0 2	1,000	100

elements are concentrated as well, among others, lead, bismuth, and arsenic. Strongly basic elements accumulate, such as lithium, and there are others, e.g., boron, which form complex anions. Consequently, the enrichment is independent of the chemical and geochemical character of the element. Another important feature is that the enrichment factors of geochemically heterogeneous elements are often of the same degree of magnitude or nearly identical.

The concentration of the elements in plant ashes is also observed in recent plants. Goldschmidt (1934, 1937*a*, 1944) has presented analyses showing the concentration of rare elements in an old forest in central Germany. His values are given in Table 8.6. Other ele-

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ments are also concentrated, for example, the rare-earth metals in hickory leaves. Table 8.6 shows, in addition, a definite concentration for boron and manganese. In these instances the concentration depends on biological factors and takes place in the living plant. However, the concentration during the decay of organic matter is more important geochemically. In this case the solutions circulating in the soil dissolve and extract inorganic compounds present in the subsoil according to their solubility. If the amount of water is small as compared with that of mineral soil, the rare elements will often be preferentially dissolved and relatively concentrated because the common elements, owing to their large amount in the soil, cannot be quanti-

TABLE 8.6
CONTENT OF SOME ELEMENTS IN MATERIALS FROM THE
FOREST AT SABABURG A.D. WESER, GERMANY

ANALYZED MATERIAL	B ₂ O ₃	MnO	NiO	GeO ₂	As ₂ O ₅	Ag	Au
	Per Cent by Weight						
Mineral soil (sand)	0 0007	0.04	0 002	0 0005			
Ashes from fresh oak leaves	0 5-1	2*	0 005	0 0005			
Ashes from oak humus . . .	0 02	0.24	0 01	0 007		0 0001	
Ashes from beech humus	0 003	0.14	0 01	0 007	0 05	0.0005	0 00005

* Ashes from fresh beech leaves. In beech leaves from the previous year 0.77 per cent MnO.

tatively dissolved in a small quantity of water. The result is fractionating leaching, the opposite of fractionating crystallization.

The solutions formed by this process enter the plant through the root system and deposit the greater part of the dissolved salts at the places of strongest evaporation, especially in the leaves. In leaves turning yellow and withering, the content of most of the minor elements decreases; and the most soluble constituents, such as alkali, alkaline-earth, and magnesium carbonates, sulfates, and phosphates and humic complexes of iron and manganese, are leached out of the decaying leaves by rain water into the deeper layers of the soil, ready to re-enter the circulation. The sparingly soluble or the insoluble constituents of other metals, e.g., hydroxides and protein and humic complexes, are retained, partly by adsorption, in the humus layer. By such simple physical processes as evaporation and filtration, recurring year after year, the plants will finally bring about the concentration of a number of elements in the topmost layers of forest

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soils, partly in the form of organic complexes, according to the solubility of the compound in question. The physical nature of the processes accounts for the fact that elements with widely varying chemical and geochemical properties become enriched. The following elements are known to become concentrated in humus soils: Ag, Au, Be, Zn, Cd, Sc, Tl, Ge, Sn, Pb, As, Mn, Co, and Ni. The concentration principle outlined above may be conveniently called the Goldschmidt enrichment principle. The concentration of elements in coal ashes was explained by Goldschmidt (1934, 1937a, 1944) in a similar way. The coals concerned are evidently analogous with recent soils rich in humus. They often form separate layers in the coal seams. It must be noted, however, that later enrichment phenomena in the coals and brown coals may be caused by circulating aqueous solutions as a result of adsorption on coal or of its reducing properties. Thus, for example, arsenic is frequently concentrated in the sulfide minerals found in coal seams.

The factor regulating the degree of the enrichment is the plant species itself. It is known that vegetation, to a certain degree, is able to become accommodated according to the chemical properties of soil. Many plants are capable of concentrating certain elements occurring in soil near or above ore bodies. They apparently give rise to progeny rich in such elements, whereas other, sensitive, plants die out (for a summary, see v. Thyssen-Bornemisza, 1942). The classical zinc pansy, *Viola calaminaria et zinci*, shows a decided activity toward zinc and accordingly grows on waste-ore dumps of zinc mines in many places in central Europe. It contains up to 4 per cent ZnO in its ashes. Other plants, like the horsetails, *Equisetum arvense* and *E. palustre*, concentrate gold, and *Viscaria alpina* and *Melandrium dioecum* endure very high copper concentrations in the soil. Vogt and Braadlie (1942) have found the latter to thrive in an ore-poisoned soil with a copper content of 6,500 g/ton, whereas the normal copper content in mineral soil is only 20 g/ton. Droplets of metallic mercury have been found in the seed capsules of *Holosteum umbellatum* growing on some mercury-rich soils.

The ability of plants to indicate the chemical properties of soil has been applied to prospecting for metal ores (geobotanical prospecting). The enrichment phenomena have also been adapted to similar purposes. Humus or plant samples are collected, and their ashes are analyzed by appropriate methods, e.g., spectrochemical analysis (biogeochemical prospecting; see Rankama, 1940, 1947b). This meth-

od was first introduced by S. Palmqvist and N. Brundin in Sweden in 1937.

Compared with plants, the animals seem to be able to concentrate only a limited number of trace elements. Copper forms a part of the molecule of hemocyanin, the respiratory pigment found in some crustaceans and in other lower animals. Copper, in the form of the proteins hemocuprein and hepatocuprein, is found in mammalian blood and liver, respectively. Vanadium is concentrated by the ascidians, for which it is essential as the chromogen in the blood. Other marine animals, like the gastropod *Pleurobranchus plumula* and the holothurian *Stichopus Moebii*, are also known to concentrate this metal from sea water. Ants are rich in manganese, which probably has some role in the formation of formic acid. Bromine as 3,5-dibromotyrosine is concentrated in some corals, and the purple snails, *Murex brandaris* and *M. purpureus*, contain bromine in the form of dibromoinidigo. In these animals bromine is concentrated from sea water. Iodine is concentrated in thyroxine, an amino acid found in the thyroid gland.

The absence of certain of the essential elements in the soil may cause regional deficiency diseases in plants, in grazing animals, and even in man. The lack of the micronutrient elements is connected with their absence in the rocks of the area in question. The elements so far studied in detail in this respect include cobalt, iron, and copper. On the other hand, the accumulation of toxic elements in plants may also be the cause of pathological conditions. This may be due either to the abundance of such elements, e.g., arsenic and selenium in rocks and soil, or to the special affinity of a particular plant for the element. Thus, for instance, many species of the genus *Astragalus* are famous for their definite association only with seleniferous soils.

Generally speaking, the geologically most ancient organisms (thallophytes, protozoans, etc.) are able to concentrate a much wider range of elements than are the highest modern animals (birds, mammals). Vinogradov (1933) has emphasized the widespread concentration of aluminum in Paleozoic flora (*Sigillaria*, *Lepidodendron*, etc.) as compared with its enrichment in only rare cases in present-day plants (*Lycopodiaceae*).

PHOTOSYNTHESIS

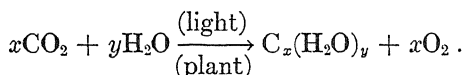
Most of the energy needed in the functions of living matter is produced by respiration, i.e., by the slow combustion of organic materi-

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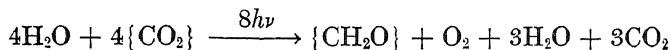
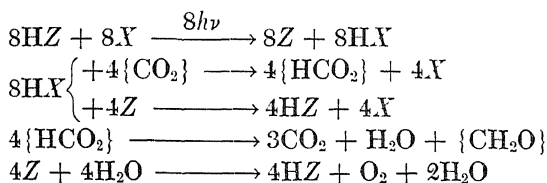
al. Organic matter is oxidized in the biosphere at a daily rate of nearly 10^9 tons. The principal products of the oxidation are ultimately carbon dioxide, water, and nitrogen. The rate of decomposition is high enough to destroy all organic matter in the biosphere in about twenty years, save for the fact that a corresponding amount of organic matter is contemporaneously synthesized.

The decomposition and regeneration of organic matter forms a part of the geochemical cycle of carbon, oxygen, hydrogen, nitrogen, and the other elements constituting the organic compounds. The chemical process by which organic compounds are formed from carbon dioxide and water is maintained by the green or chlorophyll-bearing plants. This process is called photosynthesis; it takes place under the action of sunlight and is the fundamental biochemical process, because all other reactions in plants and animals are based on the presence of previously synthesized compounds. Stable inorganic material is converted into organic compounds only through photosynthesis.

Photosynthesis is the reverse of combustion. Normal photosynthesis, which occurs in the higher plants, mosses, and algae, consists of the combination of carbon dioxide and water in organic matter, whereby oxygen is released and escapes into the medium. Basically, the over-all reaction in question can be expressed by the equation



Several mechanisms have been suggested to account for the photosynthesis. Among them, the following is at present believed to give the best illustration of the primary photochemical processes encountered (Rabinowitch, 1945):¹



1. Quoted from *Photosynthesis and Related Processes*, Vol. I, by E. I. Rabinowitch, 1945. Courtesy of Interscience Publishers, Inc.

In this scheme X is an intermediate catalyst and Z another catalyst; one of them may be chlorophyll. The primary photochemical process is an oxidation-reduction reaction between eight molecules of X and eight molecules of Z . Although there probably occur minor variations in the mechanism of photosynthesis, the general character of the process must be the same throughout the vegetable kingdom.

From the first products of photosynthesis formed in the plants a number of fats, proteins, nucleoproteins, pigments, enzymes, vitamins, cellulose, and other substances are produced. They are oxidized and decomposed before or after the death of the plant.

The chlorophyll-bearing plants are self-supporting (autotrophic) because they accumulate chemical energy. All other plants, e.g., fungi and most bacteria, are heterotrophic, being able to live only by feeding on the green plants and dissipating the energy accumulated by them. Some bacteria, called chemoautotrophic, are self-supporting; they are able to synthesize organic substances in the dark. The energy required for the synthesis is furnished by changes in unstable inorganic or organic chemical systems. In the light, the purple bacteria synthesize organic matter from carbon dioxide and hydrogen-bearing substances, such as hydrogen sulfide and fatty acids. This process is called photoreduction and is only temporarily activated by light. It is believed that the purple bacteria can exist only on account of the high chemical potential still found in some places, particularly in volcanic regions. It is possible that these bacteria were more important during the earlier stages of the evolution of the Earth, when the chemical activity on the Earth's surface was more widespread and pronounced than it is today.

The total yield of photosynthesis has been estimated, by different methods and by a number of scientists, starting with Justus von Liebig in 1840. According to Rabinowitch (1945), the most probable value of the annual rate of carbon fixation on the Earth is of the order of $15 \cdot 10^{10}$ – $20 \cdot 10^{10}$ tons, with at least four-fifths, and probably nine-tenths, of this amount contributed by the oceans. Probable values are $15.5 \cdot 10^{10}$ and $1.9 \cdot 10^{10}$ tons of carbon fixed by sea plants and land plants, respectively. Riley's (1944) estimate is about $14.6 \cdot 10^{10}$ tons annually for the whole Earth, $12.6 \cdot 10^{10}$ tons for the ocean. The comparison of this rate of carbon transformation by the plants with the total quantity of carbon available in the uppermost geospheres (see Table 19.3) reveals that the land plants assimilate, in less than ten years, a quantity of carbon equivalent to the total carbon bound

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as dioxide in the lower atmosphere. If the total carbon reserve found in the hydrosphere and atmosphere, viz., $1,700 \cdot 10^{10}$ tons, is considered, it is found that the plants assimilate a quantity of carbon equal to this reserve in less than a hundred years. This value can be checked by the annual energy accumulation by photosynthesis, which is estimated by Rabinowitch (1945) to amount to $3 \cdot 10^{21}$ cal, corresponding to the formation of $30 \cdot 10^{10}$ tons of organic carbon, a value which checks reasonably well with the estimates discussed above.

Photosynthesis forms an important part in the cycle of oxygen. The amount of oxygen in the atmosphere is approximately $120,000 \cdot 10^{10}$ tons (or 12 Gg). If the annual rate of fixation of carbon by living organisms is assumed to be $15 \cdot 10^{10}$ tons, this amount is produced from $55 \cdot 10^{10}$ tons of carbon dioxide, whereby $40 \cdot 10^{10}$ tons of oxygen are liberated. It follows that the supply of oxygen in the atmosphere must be renewed once every 3,000 years. It can also be calculated that all the water in the hydrosphere is decomposed in about $2 \cdot 10^6$ years. Consequently, all oxygen now present in the upper geospheres has repeatedly circulated in the cycle from the atmosphere through the biosphere into the hydrosphere and back during the geological history of the Earth.

GEOCHEMICAL ROLE OF BACTERIA

The very small, simple, single-celled organisms called bacteria are found to play important roles in the biosphere and the adjoining geochemical spheres. Their rate of multiplication is very high, and it is calculated that, at the rate of division once every 20 or 30 minutes, the progeny of a single spherical cell, 1μ in diameter, would produce a mass of the radius of the Earth in 3 or 4 days, provided that all survived. In the biochemical functions of the bacteria, about 30 or 40 per cent of the assimilated organic material is converted into protoplasm, whereas the rest is oxidized to carbon dioxide and water or intermediate products. Carbon monoxide may also be formed. It is likely that the carbon oxides in marsh gas are produced by bacterial action.

It is possible that a large percentage of humus and other residual organic matter in the older sediments consists of the cells of bacteria or their remains.

It is calculated that bacteria utilize organic matter at the rate of $10 \cdot 10^{-12}$ mg per cell per hour (ZoBell, 1942). In the bottom sedi-

ments, from a depth exceeding 60 or 90 cm with a bacterial population of several thousands per gram, around 10^4 years would be required from the bacteria in 1 g of the sediment for the oxidation of 1 mg of organic matter.

Although bacteria are exceedingly small, their high rate of multiplication and their high physiological activity result in their participation in chemical reactions involving considerable amounts of matter and in their importance in the geochemical cycles of carbon, nitrogen, phosphorus, and sulfur. An abundant bacterial flora is found in recent sediments deposited on the ocean bottom, ranging from hundreds to hundreds of millions per gram of the sediment, and is still met at depths in excess of 4,800 m. Bacterial activity causes a gradual decrease with depth in the organic carbon and nitrogen content of marine sediments. In general, there exists a correlation between the numbers and kinds of bacteria and the chemical composition and the physicochemical conditions of the sediments. Thus, for example, bacteria carry the main responsibility for changes in the pH of the sediments. The pH, in its turn, affects the redox potential. Some bacteria decrease the pH by producing carbon dioxide, oxidizing organic matter to organic acids, hydrogen sulfide to sulfur or sulfates, and ammonia and other nitrogen compounds to nitrites and nitrates, or by utilizing ammonia and liberating phosphates or hydrogen sulfide from proteins. A soil organism, *Thiobacillus thiooxidans*, which oxidizes sulfur may produce a pH less than 1.0. The acids produced by bacteria may dissolve calcium carbonate and other inorganic constituents from the sediments and thereby affect the cycle of calcium and the other elements considered. Other bacteria increase the pH by liberating ammonia from nitrogenous compounds, by utilizing carbon dioxide or organic acids, or by reducing sulfates and nitrates. Such bacteria favor the precipitation of calcium carbonate, especially in tropical bays with much organic matter, and the preservation of calcareous sediments.

Although bacteria do not contribute much to the mass of the sediments, most of them produce numerous enzymes or biocatalysts which may continue to be active long after the organisms are dead and which are adsorbed by the bottom sediments. The anaerobic conditions in the recent marine sediments tend to preserve the enzymes and make them available for the activation of various chemical reactions which do not take place at ordinary temperatures and pressures.

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Bacteria may have a high temperature and pressure tolerance. They thrive at the temperature from 0° to -4° C. found on the sea floor. Some species grow in hot springs with a temperature of 89° C. High hydrostatic pressures, up to 12,000 atm, are not found to limit their activity. On the other hand, the effect of the osmotic pressure is noticeable, and only a few species of soil and fresh-water bacteria tolerate salt water, although some halophilic species thrive in the most concentrated salt solutions, e.g., in the Dead Sea and Great Salt Lake, in the brines associated with petroleum deposits, and in crystallizing salt solutions of marine salterns.

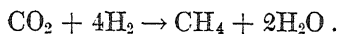
Bacteria tend to create reducing conditions or to lower the redox potential of marine sediments (see chap. 5). The aerobic bacteria thrive at higher redox potentials than do the anaerobic species, which require a low potential. Sea water may be slightly oxidizing, but the marine sediments are often more reducing than the theoretical hydrogen electrode. Anaerobic bacteria are responsible for the creation of these extremely low redox potentials. A low redox potential favors the reduction or hydrogenation of organic matter and the preservation of the reduced substances, e.g., petroleum hydrocarbons.

There are bacteria able to attack several inorganic substances and almost any kind of organic matter, e.g., proteins, sugars, starches, fats, chitin, lignin, cellulose, hemicellulose, waxes, and humic substances. Sulfate- and nitrate-reducing bacteria are usually abundant in marine sediments. There are bacteria which are heterotrophs, that is, they require organic substances as a source of carbon or energy. Autotrophic bacteria, on the other hand, obtain energy from the oxidation of inorganic substances, e.g., Fe^{2+} , Mn^{2+} , H_2S , H_2 , CO , CH_4 , and NH_4^+ . Most of the bacteria in the marine sediments, called facultative aerobes, are active in either the presence or the absence of free oxygen. The strict aerobes require free oxygen for their activities. They are less numerous; they can live only in the presence of oxygen.

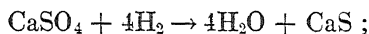
Nitrates are produced as the final stage of the bacterial breakdown of proteins. The true nitrifying bacteria are capable of fixing appreciable quantities of free nitrogen. Thereby they divert nitrogen from the atmosphere to the plants and thence to the animals. The nitrate-reducing bacteria reduce nitrates to nitrites. Other bacteria are known which oxidize ammonia to nitrites and nitrates. The nitrogen-liberating bacteria release free nitrogen from nitrates and nitrites.

Some species produce carbon monoxide and methane, some of the higher homologues of the latter, a number of aromatic hydrocarbons, and certain pigmented hydrocarbons, e.g., carotene. Other bacteria are able to utilize methane and convert it into bacterial protoplasm. The hydrocarbon-oxidizing bacteria produce carbon dioxide and bacterial protoplasm along with methane and its homologues and other organic substances. Most of the bacteria which oxidize petroleum hydrocarbons and natural gas require the presence of free oxygen or that of nitrates or sulfates as a source of oxygen.

Considerable hydrogen is produced in recent sediments as a result of the anaerobic decomposition of organic matter. The reduction of carbon dioxide by hydrogen *in statu nascendi* is believed to be the principal way leading to the formation of methane:



Sulfates are also reduced by the hydrogen:



and some hydrogen may be converted to hydrocarbons or hydrocarbon-like compounds in the hydrogenation of organic matter.

The sulfate reducers found in large numbers in recent marine sediments and oil-field waters produce sulfur or hydrogen sulfide, but the latter compound may also be formed in the bacterial decomposition of sulfoproteins. Sulfur results, in addition, in the oxidation of hydrogen sulfide by bacteria, usually in the presence of free oxygen or in light.

Carbon dioxide, in general, is the principal product of the activities of aerobic bacteria, whereas the anaerobic processes or a low redox potential result in the formation of hydrogen, hydrogen sulfide, and methane, and only minor quantities of carbon dioxide.

In recent sediments, bacteria tend to convert organic matter into more petroleum-like substances, including certain petroleum hydrocarbons. Although there is no experimental evidence indicating that they may produce crude oil, it is believed that they may promote the process in many ways (see under "Petroleum," p. 351).

One of the first changes caused by bacterial activity in marine sediments is probably the depletion of oxygen, whereby the environment becomes anaerobic. The bacteria then continue to function at the expense of other hydrogen acceptors, and thus reducing conditions are created which affect the state of iron, sulfur, manganese,

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and organic matter, especially of certain nitrogen compounds. Similarly, where all dissolved oxygen has been consumed, the hydrogen-ion concentration increased, the redox potential lowered, and toxic substances like hydrogen sulfide produced, the action of bacteria has resulted in the creation of environments inimical to other forms of life. On the other hand, bacteria also serve as important sources of food and as producers of plant nutrients.

Bacteria are also active in rock decomposition. Their presence increases the amount of inorganic constituents which are dissolved from rocks and their minerals during weathering. They liberate aluminum from hydrous aluminum silicates. Potassium is assimilated by bacteria and fungi and is consequently leached from potassium-bearing minerals. The origin of many sedimentary iron and manganese ores is attributed to bacterial activities because the hydroxides of these metals are known to be precipitated by bacteria. Sphalerite is oxidized to zinc sulfate. Zinc carbonate and silicate are dissolved by the sulfuric acid formed by bacteria which oxidize hydrogen sulfide and sulfur. Calcium phosphate, like calcium carbonate, is dissolved in acids produced by the bacterial decomposition of organic matter. Bacteria are also known to act in the transformation and precipitation of magnesium (as magnesium carbonate) and of copper and other heavy metals, particularly with the help of the hydrogen sulfide generated. There is conclusive evidence that living bacteria may occur and be active in certain sediments and sedimentary rocks of considerable geological age, as high as Permian.

ORGANOGENIC SEDIMENTS OR BIOLITHS

The role of the biosphere in the formation of independent sediments is important. The sediments resulting from the geochemical activity of the biosphere are called, according to the German naturalist, Ch. G. Ehrenberg (1795–1876), bioliths. They are best considered as a special group of sediments, because their greatest part cannot be properly included in the general classification of sediments presented in chapter 5. The classification of the bioliths, according to Potonié (1908), is given in Figure 8.4. They are divided into the incombustible acaustobioliths and the combustible caustobioliths. The former group includes organogenic limestones, continental and marine phosphate sediments, lacustrine and marine diatomaceous sediments, and still others. The latter group consists of carbonaceous sediments which contain native carbon or its oxidizable compounds.

Some sulfur deposits formed by bacteria are also included. This group contains all solid, liquid, and gaseous sediments used as fuel. The caustobioliths are consequently of high technical importance.

In Potonié's classification the caustobioliths are further divided into humites, liptobioliths, and sapropelites. The first two groups are predominantly products of land and marsh vegetation, whereas the third contains decay products of water organisms, especially plankton, algae, and small crustaceans. The nature of the sediments formed depends on the presence or absence of oxygen, this fact being of especial geochemical importance. Potonié (1908) carried out a detailed division of the processes of chemical decomposition of vegetable and animal substances leading to the formation of the causto-

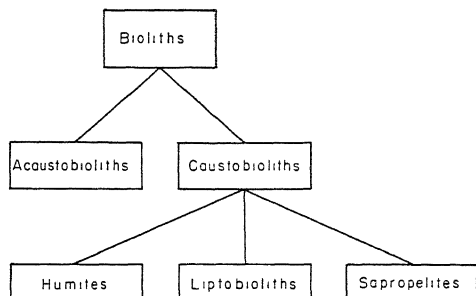


FIG. 8.4.—Classification of the bioliths

bioliths. According to this author, the disintegration (*Verwesung*) of the organisms has more or less the nature of a slow combustion process, provided that an adequate supply of oxygen is present, e.g., in oxygen-bearing surface waters of lakes and seas or on the Earth's surface under the direct action of oxygen and water. Under these circumstances only volatile oxidation products will be formed: carbon is oxidized to carbon dioxide and hydrogen to water, and sulfur yields SO_3 and sulfates, whereas nitrogen escapes into the atmosphere or forms NO_3^- or NH_4^+ ions, which are soluble in water. No residue of solid carbon compounds, i.e., no coal, is produced. Only a small part of the organic matter, such as resins and waxes which are not easily decomposed, remains unchanged and sometimes forms caustobiolithic residual sediments or liptobioliths. If the supply of oxygen is inadequate, the decomposition is incomplete and results in the formation of small amounts of carbon-bearing substances, such as the black mold formed in moist forests during fall. This process is called moldering (*Vermoderung*). With the decrease in the amount of oxy-

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gen present during the decomposition, the character of the resulting sediments will change still more. Peat formation (*Vertorfung*) is the next stage; it is intermediate between molding and putrefaction. There is an oxygen deficiency present at the start of the peat formation, and during the later stages of the process this element is completely absent. The decomposition takes place in stagnant waters. Peat is a typical humite sediment of vegetable origin. In it the original structure of the plant remains is often still partly visible. Humus is the final product of peat formation. During all these processes bacteria and fungi participate in the decomposition.

If no oxygen is present at all, the process of putrefaction (*Fäulnis*) will take place. Sapropelites are formed as its final products. They are typically lacustrine or marine sediments formed in stagnant waters where there is no addition of water charged with oxygen. The putrefaction of the remains of plankton, algae, and small crustaceans living in water is of high importance in the formation of sapropelites. These organisms contain more proteins, fats, oils, and waxes than does land vegetation, and therefore their decomposition products differ from the humite sediments. Putrefaction is a kind of slow distillation, and during the decomposition in reducing environments, which is generally aided by bacterial action, the above-mentioned organisms, together with spores and pollen grains which are usually present, yield chiefly methane, along with other hydrocarbons, hydrogen sulfide, ammonia, hydrogen, carbon dioxide, and a number of organic compounds. Both carbon and nitrogen become enriched during this process and fatty substances as well, if originally present. The sapropel or foul mud formed as a result of the decay often contains notable amounts of sulfides, which have an important effect on the minor cycle of many sulfophile metals. The latter are precipitated as sulfides and are thus removed, to a large degree, from the hydrosphere. If the chemical decomposition of organic substances is carried still further, petroleum will result as the end-product (see under "Petroleum," p. 351).

It must be emphasized that humus is formed through the decay of land and marsh vegetation, whereas sapropel is a product of putrefaction below the surface of water in swamps, stagnant lakes, and sheltered places along the seashore. Only these two processes are of importance in the formation of coal because large quantities of organic substances are preserved only under these conditions. However, it might also be possible that the differences between humus

and sapropel are not primarily due to their formation by different processes but to differences in the degree of decomposition and, above all, to a difference in the composition of their mother-substances (Stutzer, 1923, 1940).

HUMUS

During the cycle of organic matter in the biosphere the plants and animals, upon their death, are attacked by micro-organisms, whereby the substances synthesized by the living organisms are decomposed and return to the cycle. However, some residues are more or less resistant to microbial decomposition and accumulate, thus giving rise to substances called humus. The main geochemical importance of humus lies in the fact that by its formation a part of the elements indispensable for organic life, especially carbon, nitrogen, phosphorus, sulfur, and potassium, are removed from their geochemical cycles. Because only limited quantities of carbon, combined nitrogen, and phosphorus are available for plants, the formation of humus regulates the plant life. Humus thereby acts as a reserve and stabilizer of organic life. The amount of organic matter conserved in humus is very much greater than that bound within all living systems of the biosphere.

Humus is composed of a highly complex mixture of amorphous organic substances, which consist partly of residual animal, vegetable, and microbial substances, and partly of matter formed during the decomposition of the above-mentioned substances by the action of micro-organisms. The carbon content of humus usually ranges from 55 to 56 per cent. The content of nitrogen is considerable, commonly 3–6 per cent. The presence of nitrogen is one of the most important and characteristic chemical properties of humus. The C:N ratio in humus is close to 10:1 but varies according to the stage of decomposition. Some inorganic constituents, containing P, S, Fe, Ca, and Mg, form an essential part of humus, which has no definite chemical composition but changes constantly because of the continuous decomposition. A large number of organic compounds are present, some of which were already contained in the original plant and animal residues, whereas others were formed by the bacterial decomposition of the residues, and still others were synthesized by the micro-organisms.

The role of the micro-organisms in the cycle of organic matter in Nature is very important. In the formation and transformation of

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humus, in which these organisms find a natural habitat, they are the primary agents. Various groups of micro-organisms produce carbon dioxide, ammonia, nitrates, and sulfates during the decomposition of organic matter. Consequently, the elements which are most important for the growth of plants, especially carbon and nitrogen, are kept in constant circulation. These elements and other plant nutrients, like phosphorus, calcium, iron, manganese, and still others, are stored in humus for considerable periods of time. Humus, by its effect on the hydrogen-ion concentration and the oxidation-reduction system of the soil and by its capacity to adsorb certain toxic compounds therein, influences the growth of plants.

Humus forms a complex colloidal system. It is practically insoluble in water but able to form colloidal solutions. In soil it is found to combine with the inorganic clay fraction, whereby colloidal compounds are produced. Because the humus particles are negatively charged, they adsorb positive ions of the electrolytes present in solution and form humic compounds frequently called "humates." The alkali "humates" are readily soluble, whereas those of calcium and magnesium are less soluble or dispersible, and the humic compounds of Al^{3+} and Fe^{3+} are insoluble or nondispersible at the isoelectric point. The aluminum and iron compounds, on the other hand, become readily soluble with changes in pH; they are distinctly amphoteric. The phenomena of base adsorption and base exchange in humus solutions are explained by the properties just discussed. The water and nutrient salts adsorbed by humus are of much importance in agriculture because the major microbiological activities take place in the colloidal humus system.

The humus-bearing solutions increase the solubility of detrital minerals in soil and rocks, whereby such elements as iron and manganese are brought into solution in the form of humic complexes. Hence humus is of importance in the weathering of rocks. The influence of humus on this process is twofold. First, the carbon dioxide liberated from humus during microbial activity or chemical reactions acts as a dissolving agent for the minerals by increasing the hydrogen-ion concentration of water and thereby activating the chemical weathering. In the case of calcium and the other alkaline-earth metals and probably also of iron and manganese, bicarbonates which are readily soluble may also be produced. Second, the humic complexes, owing to their capacity to exchange and adsorb cations, play a role in the rock disintegration. Gruner (1922) has studied the solu-

bility of various minerals and rocks in peat solutions. He found that solutions from decaying plant remains dissolved all oxide and carbonate minerals of iron but did not seem to attack pyrite. In the presence of sea water or other chloride- and sulfate-bearing waters the dissolving action of peat solutions was greatly increased. The presence of carbonates in the natural organic solutions was found to impede the dissolution of silica. The organic solutions reduced ferric compounds to soluble ferrous salts, whereas carbonic acid did not possess this property. According to Blanck (1933), the organic complexes of humus do not, contrary to previous belief, participate in the chemical disintegration as such; the activation is due to sulfuric and nitric acid and their salts, formed during the decomposition of humus, because the amount of the humic substances formed is too low to be of much importance. Sulfuric acid is an abundant constituent of forest humus, bog waters, and soils formed during chemical weathering.

In mineral soils the presence of humus is responsible for conditions favoring the growth of plants. It plays an essential part in the soil formation, and the soil is affected in many ways by the humus content. Humus is an important mother-substance of peat and coal (see under "Coal," p. 349). The mechanism of the formation of humus in soil is presented in Figure 8.5, which is based on Waksman (1936).

Various forms of humus, called water humus, are produced under water. They are chemically similar to soil humus, although their carbon and nitrogen content is lower. The bottoms of rivers and lakes become covered with a layer of mud, called sapropel, which is rich in nitrogen and phosphorus and able to adsorb potassium and calcium. The accumulated water humus may be later converted into peat.

Very considerable amounts of humic substances are brought into the sea by rivers and streams (see chap. 6). Still greater quantities of organic matter are synthesized by marine organisms, which, upon their death, sink to the bottom and are decomposed by micro-organisms. The importance of marine humus lies in the fact that it is the only source of food for benthic animals and bacteria. The presence of organic matter and the changes produced by biological activity influence the marine sedimentation and also the nature of the sediments. Carbon, nitrogen, and probably also other elements are, at least temporarily, removed from their cycles during the formation and burial of marine humus. The marine bottom deposits produced are usually classified in two groups: the pelagic deposits, formed in deep water and at a great distance from land, and the terrigenous muds, deposit-

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ed close to land. The first group consists of the radiolarian, diatom, globigerina, pteropod, and coccolith oozes and the red clay, and the terrigenous deposits include muds of various colors, which contain appreciable amounts of organic matter and colloidal hydrous ferrous sulfide. So far, little is known of the chemical composition of the organic matter in marine sediments. Some analyses are given in Table 8.9.

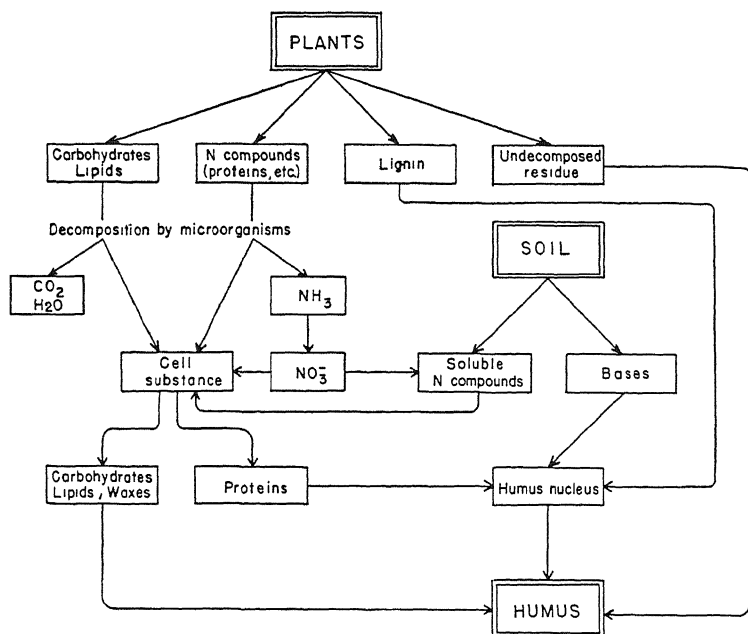


FIG. 8.5.—The formation of humus in the soil. (Based on material from *Humus*, by S. A. Waksman, 1935. Courtesy of The Williams & Wilkins Company.)

Ammonia is produced during the decomposition of soil humus, and it is gradually converted into nitrates. The bulk of the ammonia found in the atmosphere and rain water comes from soil. Other elements—carbon in the form of carbon dioxide, phosphorus in phosphates, and sulfur in sulfates—are also liberated during the decomposition. These compounds, being present in a form readily available for the growth of plants, influence the fertility of the soil and form a supply of elements essential for the synthesis of new organic substances by plants. Therefore, a large proportion of the carbon needed for physiological processes and most of the combined nitrogen and other nutrients required for the growth of plants are stored in humus.

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This substance is also a source of vast quantities of fuel. Consequently, the importance of humus in the human economy is obvious.

COAL

Sapropel and peat are accumulations from which coal is formed. It is now believed that lignin is the chief mother-substance of coal. Peat, brown coal, and the different varieties of coal are the most important humite sediments. The chemical changes connected with their formation are presented in Table 8.7, which is based on F. Muck's analyses as quoted by Stutzer (1923).

There is no sharp distinction between peat and coal. Carbon, hydrogen, oxygen, and nitrogen participate in the coalification. During

TABLE 8.7
AVERAGE CHEMICAL COMPOSITION OF HUMITE SEDIMENTS

MATERIAL	C	H	O	N
	PER CENT			
Wood fiber	50	6	43	1
Peat.....	59	6	33	2
Brown coal.....	69	5 5	25	0 8
Bituminous coal....	82	5	13	0 8
Anthracite	95	2 5	2 5	trace

this process, which finally results in the formation of anthracite, the content of carbon increases, whereas that of hydrogen, nitrogen, and, especially, oxygen decreases. The content of hydrogen and oxygen, calculated on the basis of the carbon value 100, is given in Table 8.8, which is based on Stutzer (1923). The changes in the oxygen and hydrogen content are due to the formation of carbon dioxide and water; carbon monoxide and free oxygen are formed only in subordinate amounts during the decomposition of organic matter. A part of the nitrogen is also released and escapes as free N_2 . Hydrogen is partly removed as methane, CH_4 , which forms the bulk of the dangerous explosive firedamp in coal mines.

The coals can be divided into two groups according to their origin, viz., humic coals and sapropelic coals. The cannel coals and Boghead coals (torbanite), representing the latter group, are high in bitumen. The cannel coals contain many spores, whereas the Boghead coals are of algal origin. Various transitions are present between the sapropelic coals and from them to oil shales and humic coals.

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On the whole, the chemical constitution of coal is very complex, and the information concerning it is still scarce. It is now known that no free carbon is present in coal. Plant components or secretions which are resistant to decay are important constituents of coal, and humic substances also compose a considerable part of many coals. The coals are essentially colloidal and consist of solid complex compounds of carbon, hydrogen, and oxygen. The content of nitrogen is small. Other more important constituents include sulfur and phosphorus. Most of the former element has its origin in the sulfur found in the original plant material. During the decay of the plant substance hydrogen sulfide may be generated, which precipitates iron as sulfide. Bacteria may also deposit iron as sulfide, and the reduction

TABLE 88
CONTENT OF HYDROGEN AND OXYGEN IN
HUMITE SEDIMENTS
(C = 100)

Material	C	H	O and N
Wood fiber . . .	100	12	88
Peat	100	10 2	59 2
Brown coal	100	8	37 4
Bituminous coal ..	100	6	16 8
Anthracite.	100	2 6	2 6

of iron sulfate to sulfide by coal is possible as well. Sulfide sulfur (pyrite, marcasite) is the most important form of sulfur in coal. Organic sulfur is also commonly present, whereas sulfates (gypsum) and native sulfur are rare. Sulfides of lead, copper, zinc, nickel, and other metals are incidental constituents of coal. The high phosphorus content of cannel coal is largely attributed to the high spore content.

Silicon, aluminum, and iron are the main constituents of coal ashes. Other constituents include Ti, P, Ca, Mg, Na, K, and S. The presence of rare elements in coal ashes was discussed in a previous paragraph.

The gases inclosed in coals consist mainly of nitrogen, methane, and carbon dioxide. Free hydrogen in small quantities is a probable constituent. Nitrogen is derived mostly from the air. During weathering, the amount of nitrogen and carbon dioxide and of ethane and the higher hydrocarbons increases, whereas that of oxygen and methane decreases. The analysis of gas from a coal mine is presented in Table 8.12.

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A continuous change in the chemical composition of the plant material takes place after its deposition, and peat, brown coal, bituminous coal, and anthracite represent different stages of the progress of the incoallation or the coal formation (*Inkohlung*). This process begins when the peat formation is completed, but there is no sharp boundary line between the two. The brown coals are usually found in geologically young formations, especially in those of Tertiary and Mesozoic age, whereas the coals proper belong mostly to Paleozoic formations. However, brown coal is sometimes encountered in Paleozoic deposits, and coal seams may be found in sediments as young as Tertiary. These exceptions to the general rule make evident that the difference between brown coal and coal is not due to their differing geological age. It is caused, instead, by the conditions existing during the incoallation, especially by temperature. Elevated temperatures, such as are likely to prevail in orogenic zones and their neighborhood, are found materially to accelerate the incoallation, even in the case of geologically young formations, whereas humite sediments at localities more remote from the metamorphosed areas are often preserved in the form of brown coal.

Changes in the composition of coal arise also during its weathering, i.e., the slow combustion caused by atmospheric oxygen. During these changes the content of carbon, hydrogen, sulfur, and phosphorus decreases but that of oxygen and nitrogen increases. A process of hydrocarbon enrichment (*Bituminierung*) follows after putrefaction. Coals rich in bituminous substances are thereby produced.

LIPTOBIOLITHS

The name of liptobioliths refers to their resistance to decomposition. Waxes, resins, fats, and oils contained in small quantities in many organisms are able to resist chemical decomposition for considerable periods of time. They become concentrated, consequently, and may affect the composition of the caustobioliths. They are responsible for the characteristic properties of sapropel and sapropelic coals. Even peat may sometimes contain considerable amounts of the above-mentioned substances. The liptobioliths include, for example, resin and wax coals (pyropissites), pollen and spore coals, the subfossil copal gum, and the fossil amber or succinite.

PETROLEUM

Petroleum is found on every continent, with the exception of Australia. It is a complex mixture of liquid hydrocarbons in which a num-

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ber of gaseous and solid hydrocarbons are dissolved. Their range in chemical composition is given by ZoBell (1945) as shown in the accompanying tabulation.

	Per Cent
C.....	82.2-87.1
H.....	11.7-14.7
S.....	0.1- 5.5
N.....	0.1- 1.5
O.....	0.1- 4.5
Inorganic substances	0.1- 1.2

The constituents of crude oils are divided, according to Hlauschek (1937), into several classes with reference to their chemical properties, the most important of which are:

1. Paraffin hydrocarbons, C_nH_{2n+2} , aliphatic, saturated chains
2. Cycloparaffin or polymethylene hydrocarbons (the naphthenes), C_nH_{2n} , alicyclic, saturated rings
3. Benzenoid hydrocarbons, C_nH_{2n-6} , aromatic, unsaturated rings

The following hydrocarbons are usually met only in small amounts or in traces:

4. Olefin hydrocarbons, C_nH_{2n} , aliphatic, unsaturated chains
5. Diolefin hydrocarbons, C_nH_{2n-2} , aliphatic, unsaturated chains
6. Acetylene hydrocarbons, C_nH_{2n-2} , aliphatic, unsaturated chains

Besides the hydrocarbons, the crude oils carry numerous organic substances, containing nitrogen, oxygen, phosphorus, and sulfur. These constituents are present in small quantities. They include fatty acids, phenols, naphthenic acids, resinous compounds, and asphaltenes. Sulfur compounds, like mercaptans, thiophenes, sulfones, sulfoxides, sulfonic acids, and organic sulfides are found. The nitrogenous compounds include pyridines and quinolines and still others. Hydrogen sulfide, carbon dioxide, and nitrogen are usually encountered only as minor constituents in the crudes. The sulfur compounds are sparingly volatile and consequently are concentrated particularly in the higher fractions and residues of the oil. Free sulfur associated with petroleum deposits is rather uncommon. Hydrogen has never been met in crude oil. Radon tends to concentrate in petroleum, but the content of radium is very small. Small amounts of optically active substances known to occur only in plants and animals are also found in the crudes. With few exceptions, petroleum and the various bituminous substances also contain pigments of the porphyrin type, formed from the coloring matter of animals (hemochromogen) and

the green coloring substance of plants (chlorophyll). Many metals, notably nickel, vanadium, lead, and iron, are also found in petroleum, perhaps in the form of metal-organic porphyrin compounds. The content of metals may be appreciable. A Mexican crude oil is reported to contain 240 g/ton nickel (Krejci-Graf, 1930), and up to nearly 75 per cent vanadium pentoxide may be present in some oil ashes. According to Egloff (1933), the following elements are also found in crude oils: Na, Mg, Ca, Al, Si, Ti, U, Mn, Co, Pt, Cu, Ag, Au, Zn, Sn. Heide (1938) has found, among others, Ba, Cr, Ga, Be, Cd, As, Ge, Li, P, Mo, and the platinum metals in the ashes of some German crudes.

According to Goldschmidt (1937*a*, 1944), the characteristic assemblage of elements associated with oil and asphalt and also with bituminous shales is the following:

V, Ni, Mo
(Cu, Ag, W)

The first three elements are the most effective catalysts for the industrial synthesis of hydrocarbons. Goldschmidt suggests that valence forces might control the association between the above metals and natural hydrocarbons.

Vinogradov (1943) has established the presence of regional variations in the vanadium content of certain oil-bearing regions in Russia, some of which show an extremely high concentration of this metal in the crudes, whereas it is totally absent in other provinces. Vinogradov concludes that vanadium was concentrated from marine muds into the protopetroleum. Owing to its catalytic activity, vanadium has determined the later character of the Russian crudes, which, as a rule, have an asphalt base with a high sulfur content.

Few, if any, of the petroleum hydrocarbons are unsaturated, and they all are optically active. The complex and labile character of the crude oils is responsible for the fact that no complete chemical analysis of them has ever been made.

The crudes show a varying chemical composition according to the substances from which they were formed. Hlauschek (1937) thinks that the chemical character of the mother-substance of petroleum may have changed continually during geological evolution. He assumes, in addition, the presence of periodic changes of the circumstances of decomposition which affect the composition of the mother-substance. Consequently, it is readily understood that the crude oils from different oil fields differ widely in their physical properties and

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chemical composition. Thus, for instance, the Caucasian oils in Russia consist mostly of naphthenes, whereas the Pennsylvanian crudes in the United States belong nearly completely to the paraffin series. Some crudes from Borneo are rich in benzene and toluene. According to Hlauschek (1937), the naphthene oils lie on top of the methane oils if the two occur in the same field. Among Paleozoic oils, the methane oils preponderate; but in younger crudes the abundance ratio grows more even, and, among the late Tertiary oils, the naphthene oils are found to predominate slightly over the methane oils.

Petroleum is now generally believed to be a product of decomposition of organic substances present in sapropelic sediments or muds in primary marine environments. The mother-substance of petroleum consists evidently of remains of plants and animals, partly of marine origin and partly carried to the sea by rivers. The most favorable mother-substances of petroleum are organic compounds deficient in oxygen. Preserved hydrocarbons, originally found in various plants and animals, might also account for some of the petroleum. It is estimated that an average of 0.02 per cent of the solid substances produced by plants consists of hydrocarbons. The presence of nitrogen, optically active substances, and pigments in petroleum is considered an important proof of its organic origin. The porphyrin compounds found in oil shales and asphalts are considered evidence of the presence of vegetable matter in the source sediments.

It is believed that the organic mother-substance of petroleum was deposited in near-shore sediments under essentially anaerobic conditions. Phytoplankton is the main source of organic matter in sediments. The organic substances which accumulate therein consist mainly of the resistant waste products resulting from the consumption of plankton organisms by other organisms. According to Trask (1936), the recent marine sediments contain, on an average, 2.5 per cent of organic matter by weight. The amount varies in near-shore sediments from 1 to 7 per cent. Some Black Sea deposits contain as much as 35 per cent organic matter. In ancient sediments from Cambrian to Pliocene the average content of organic matter is 1.5 per cent by weight (Trask, 1936). With reference to the loss in organic matter during the burial of the sediments, it may be concluded that an original content of at least a few per cent of organic substance in sediments is required to cause the formation of oil deposits of economic value. Petroleum is probably not generated until the sediments have been buried for some time.

Geological evidence shows that petroleum has been formed at low temperatures, probably less than 150°C. , and that no substantially elevated temperatures have been encountered during its further evolution. It was previously suggested that the transformation of the organic material was caused by temperature or pressure metamorphism. However, no residue from a dry distillation has ever been found. It is consequently now generally believed that the organic matter was decomposed by bacteria, although thus far only methane has been proved to result from bacterial action. The presence of ethane and propane and traces of higher hydrocarbons in firedamp, swamp gas, and sewage gases suggests the biogenic formation of higher hydrocarbons. In addition, Sturm and Orlova (1937) have found that a liquid petroleum-like hydrocarbon, balthashite, is anaerobically produced from fats and palmitic acid. However, no traces of liquid hydrocarbons have, as yet, been reported to be present in recent sediments.

It is known that large populations of biochemically active bacteria are distributed in recent marine and lacustrine sediments and in reservoir fluids from oil wells and that they are able to utilize or transform nearly all kinds of organic matter. They also attack several inorganic substances. The organic matter in the recent sediments consists of the decomposition products of fats, proteins, and carbohydrates originally present therein. When the organic substances are decomposed during the formation of petroleum, the action of bacteria evidently takes place along with the work of geological, physical, and chemical factors. The information now available shows that bacteria in recent sediments tend to transform organic matter into substances which are more petroleum-like than the mother-substances were and which consist primarily of carbon and hydrogen. The content of oxygen, nitrogen, phosphorus, and sulfur in the organic matter is thereby reduced, whereas that of carbon and hydrogen increases, as is shown by the analyses in Table 8.9 of the average proximate composition of organic matter in sediments of increasing age, published by ZoBell (1943).

The oil-bearing sediments are usually highly reducing. The low redox potentials created by bacteria and allied micro-organisms in certain environments favor the hydrogenation of organic matter and the preservation of petroleum hydrocarbons. Once created, the reducing conditions are maintained by certain organic compounds, ferrous iron, reduced manganese, hydrogen sulfide, and other inorganic

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constituents of sediments. Recent marine sediments, which are more reducing than the theoretical hydrogen electrode is, are rather common (ZoBell, 1946*b*). In oxidizing environments the organic matter is likely to be carbonized or oxidized by micro-organisms to carbon dioxide and water.

Certain sulfate-reducing bacteria, by producing hydrogen sulfide, may create reducing conditions which favor the formation and preservation of petroleum hydrocarbons. However, some sulfate reducers attack petroleum and modify its composition. Although some oils possess bacteriostatic properties, nearly a hundred species of bacteria, yeasts, and molds are able to alter the composition of the crudes. They attack preferentially the paraffin hydrocarbons (ZoBell, 1946*c*).

TABLE 8.9
AVERAGE PROXIMATE COMPOSITION OF ORGANIC MATTER IN SEDIMENTS

SOURCE OF ORGANIC MATTER	C	H	O	N	P
	Per Cent				
Marine sapropel	49	5	40	3.4	0.8
Recent sediments	58	7	34	2.2	0.6
Ancient sediments	73	9	14	0.9	0.3
Crude oil	85	13	0.5	0.4	0.1

According to ZoBell (1942), the occurrence of lipolytic bacteria, which utilize the glycerol from fats, leaving long-chain fatty acids, may offer clues for the interpretation of the genesis of petroleum.

Conditions inimical to the activity of micro-organisms appear to be prerequisite to the accumulation of petroleum hydrocarbons in recent sediments (ZoBell, 1946*c*). However, the accumulation of the hydrocarbons may also be prevented by bacteria which destroy and oxidize the hydrocarbons, whereby carbon dioxide is always formed as the principal product.

The release of oil from sediments is another important function of bacteria in the accumulation of oil in subterranean deposits. The bacterial and other enzymes or biocatalysts, even after the death of the micro-organisms, must also be considered to be of importance in the formation of petroleum.

Berl (1940) claims that oil, asphalts, natural gas, and bituminous coal have been formed mostly from the main constituents of many

vegetable substances, viz., carbohydrates and their derivatives. He also thinks (Berl, 1941) that sulfur and nitrogen in asphalts and oils are partly relics of the proteins found in the original plant material, whereas another part of sulfur may come from sulfur-bearing mother-rocks. He believes that the role of bacteria is small and that the carbohydrates with an initial content of approximately 50 per cent oxygen lose this element during complicated intramolecular combustion or hydrogenation, leading to the subsequent formation of humic acids, protoproducts, asphalt, and, finally, crude oil, which is oxygen-free. A part of the necessary hydrogen is thought to be furnished by hydrogen sulfide obtained from gypsum and anhydrite, whereby sulfur is formed as a by-product. The asphalts produced during the transformation contain about 10–14 per cent oxygen, which may be replaced by sulfur without changing the nature of these compounds. Heck (1941) has expressed the opinion that the hydrogen present in the organic matter of sediments is inadequate to balance hydrogen in the formed hydrocarbons and that additional hydrogen is produced, e.g., by the reduction of calcium sulfate to sulfide, which reacts with siderite and water, producing pyrite and hydrogen, among other substances.

It is possible that hydrogen sulfide is a by-product of the formation of petroleum. The occurrence of sulfate-reducing bacteria in marine sediments and associated with petroleum and oil-well waters and the presence of FeS in recent and FeS_2 in fossil bituminous rocks seem to favor this opinion.

Another possibility of the formation of additional hydrogen needed in the hydrogenation is furnished by certain bacteria which are able to produce hydrogen by the anaerobic decomposition of organic matter.

Later important changes in the composition of petroleum may be caused by radioactivity. Bell, Goodman, and Whitehead (1940) have discussed the cracking of petroleum hydrocarbons by α -rays. The radioactivity of the crude oils investigated was found to be quantitatively sufficient to cause appreciable cracking by these rays during geological time. These reactions, along with subsequent hydrogenation, may therefore considerably change the composition of the crudes. The sulfur content and the nature of the associated sediments may also have had some effect on the composition of the crudes, as well as the presence of some metals with catalyzing properties.

Water is found in connection with most of the petroleum deposits

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either in the oil-bearing beds or in the neighboring ones. Fresh water is uncommon and, if present, is descending surface water. Salt water is common and important. These brines are, both geologically and genetically, related to the petroleum deposits. They are mainly chloride waters, but near the surface sulfide waters may also occur, formed by the reduction of CaSO_4 . The primary constituents include NaCl , H_2S , KCl in varying amounts, and small quantities of CaCl_2 and MgCl_2 . Iodine and bromine are characteristic constituents. The amount of sulfates and carbonates is very low. Ammonium salts and phosphates are sometimes met. The content of iron is low. Boron is reported to be present in some brines.

It was previously suggested that the brines represent connate waters or fossil waters, i.e., primary sea water trapped in the sapropelic sediments during their deposition. The infiltration of salt water from near-by salt deposits was also considered a possible explanation of their origin. However, it was suggested by Mrazec (1926) that the iodine found in the brines is of organic origin because sea water is practically free of this element. A similar conclusion may be based on the sometimes very high potassium content of the brines. Consequently, Krejci-Graf (1930) suggested that the high iodine and potassium content is due to marine organisms and that the brines are formed by the same processes which are responsible for the formation of petroleum. The biophile character of iodine and bromine and the high content of potassium in many marine organisms furnish additional proof of this hypothesis. Considerable geological and chemical evidence was offered by Krejci-Graf to show that the connate-water and the infiltration hypotheses cannot be accepted. Thus, for instance, the salt concentration of the brines is often very high. The evaporates are practically free of iodine, and only in exceptional cases may the salt beds contribute to the brines. Krejci-Graf emphasized the fact that plankton organisms are rich in water and may often contain more than 90 per cent water. Hence, particularly during the early stages of the formation of petroleum, when the source sediments are deposited, a considerable part of the organic matter is decomposed to form water and carbon dioxide, and the oxygen originally present is used up in these reactions. The water which is formed acts as a solvent for the other products of decomposition. Consequently, the explanation of the considerable content of potassium, bromine, and iodine in the brines is that the inorganic constituents of the organic matter became separated and dissolved in water. The con-

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tent of iodine in the brines and their high salinity suggest that enrichment procedures have been active during their formation. According to Krejci-Graf, the brines are the main product of petroleum formation, whereas oil occurs only in subordinate amounts.

The composition of the brines departs decidedly from that of sea water. Krejci-Graf (1930) presents an analysis, showing the average composition of Rumanian Pliocene (*Müot*) and Miocene (*Salzformation*) brines (Table 8.10).

TABLE 8.10
AVERAGE CHEMICAL COMPOSITION OF SALTS FROM
SOME RUMANIAN BRINES AND FROM SEA WATER*

CONSTITUENT	BRINES	SEA WATER†
	Per Cent	
Na	32.85	30.17
Ca	6.45	1.14
K	5.67	1.09
Mg	3.99	3.63
Fe	0.189	max. 0.00006
Cl	50.40	54.23
Br	0.474	0.19
I	0.024	0.00014

* Partly based on material from *Geochemie der Erdöllagerstätten erläutert an den rumänischen Vorkommen*, by Karl Krejci-Graf. Copyright 1930 by Wilhelm Knapp, Verlagsbuchhandlung. Used by permission.

† Composition calculated from Table 6.17, assuming a salinity of 35 parts per thousand.

The small content of magnesium and potassium and the high value of calcium are explained as possible results of the migration of the brines together with petroleum. The comparison of the composition of the brines and that of sea water shows that the brines are higher in iodine and often also in potassium. In addition, the calcium content of the brines is higher than that of magnesium, whereas the case is the reverse in sea water. The brines do not carry notable quantities of sulfates, which are, on the other hand, always present in sea water. The absence of the sulfates in the brines is due to the reduction to sulfides caused by bituminous substances.

Paneth (1938) points out that the brines connected with petroleum contain up to 10^{-10} g/ml radium, whereas the content in surface waters and sea water is only approximately 10^{-15} g/ml and in the so-called radioactive springs usually not more than 10^{-13} g/ml. The high

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radioactivity of these springs is due to radon. It is very probable that the high radium content is closely connected with the low content of sulfates in the brines, because RaSO_4 is very sparingly soluble, and only water with less than 0.2 per cent sulfate is able to dissolve radium salts. The absence of sulfates in the brines has apparently enabled them to dissolve radium compounds from the surrounding rocks.

OZOCERITE AND ASPHALT

Ozocerite and asphalt are often found together with petroleum. They are usually thought to represent solid oxidation and polymerization products of the crude oil, formed during its weathering. The occurrence of ozocerite is connected with that of the paraffin oils; it is a mixture of solid hydrocarbons. Asphalt is frequently met as an oxidized residue in oil fields. Some asphalts are remarkably rich in vanadium and nickel; for instance, an asphalt from Argentina is reported to contain 38.2 per cent vanadium in its ashes (Krejci-Graf, 1930), and some asphalts from Trinidad and Switzerland and certain North American crude tars are high in nickel. Because the sulfur compounds found in petroleum are only slightly volatile, they tend to become concentrated in asphalt.

The asphalts contain oxygen and are, in this respect, similar to tars found in oil-bearing rocks in Venezuela, Arabia, and Iraq. According to Berl (1940), most of the asphalts and tars are intermediate products in the formation of petroleum.

NATURAL GAS

The gases occurring in Nature may be divided into three groups:

1. Inorganic gases
2. Gases produced by carbonization in the biosphere
3. Gases connected with petroleum deposits

The first group contains the gases found in pores and cavities of rocks and their minerals, the occluded gases, the volcanic gases, and those dissolved in mineral wells and springs—in all, gases connected with igneous activity. Gases belonging to this group were discussed in chapter 5. The second group includes the marsh gas and the gases found in coal mines. The third group incorporates the natural gases proper, which are usually defined as pertaining to the most volatile of the constituents of petroleum. They fill pores, cavities, fissures, and fractures in the petroliferous sediments and sedimentary rocks of all geological ages, being concentrated in the uppermost parts of

the oil-bearing beds. These compounds occur in the gaseous state under the circumstances usually met on the Earth's surface. Most of these gases are of organic origin.

Commercial supplies of petroligenic natural gas are found within structurally closed parts of reservoir rocks, as deep as 3,500 m or more. The chief constituents of these gases are highly volatile hydrocarbons, viz., methane and its homologues, unsaturated hydrocarbons, and olefins. Varying quantities of other gases appear to be present as normal constituents of petroligenic natural gases: nitrogen, oxygen, carbon monoxide and dioxide, hydrogen sulfide, helium, and hydrogen. Helium is usually scarce and hydrogen rare. The presence of hydrogen is explained by the hypothesis of the cracking of natural hydrocarbons by α -rays, whereby hydrogen is generated. Radon and argon are also sometimes met in the gases. It is believed that nitrogen and argon are remains of air consumed in the oxidation of bituminous substances.

The petroligenic natural gases are divided into hydrocarbon, nitrogen, carbon dioxide, and helium types (Ley, 1935). Many of the rich nitrogen gases are rich in helium as well. Some oil-field and natural gases are known to be extremely rich in hydrogen sulfide; a gas from Texas in the United States is reported to contain as much as 20.50 per cent H_2S . Analyses of natural gases rich in helium and nitrogen and of those rich in carbon dioxide from American localities are presented in Table 8.11, which is based on analyses collected and published by Dobbin (1935).

The gaseous hydrocarbons found at ordinary temperatures and pressures are principally methane, CH_4 , and ethane, C_2H_6 ; but varying quantities of propane, C_3H_8 , and butane, C_4H_{10} , may also be present. If present, the higher members up to heptane, C_7H_{16} , and still others occur as vapors.

The content of helium in natural gas may be as high as 16 per cent. Rich helium and nitrogen gases occur in Kansas, Ohio, Texas, Colorado, and Utah in the United States in formations ranging from Cambrian to Tertiary. Actually only the gas fields in the United States yield gas sufficiently high in helium to warrant its extraction on a commercial scale. It is believed that helium in some natural gases, at least, is produced by the disintegration of radioactive elements present in the relatively close-lying basement rocks.

Deep wells containing gas rich in carbon dioxide occur mainly in western United States and in Mexico. The carbon dioxide probably

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originated during the metamorphic alteration of the relatively shallow-lying basement rocks, by the oxidation of hydrocarbons brought into contact with mineralized waters, by the action of hot magmas on limestone, and by eruptive aftereffects (Dobbin, 1935).

The soil above subterranean petroleum deposits contains hydrocarbons, which are slowly escaping from the oil. The use of hydrocar-

TABLE 8.11
ANALYSES OF NATURAL GASES RICH IN HELIUM,
NITROGEN, AND CARBON DIOXIDE

SOURCE AND LOCALITY	CH ₄	C ₂ H ₆	CO ₂	O ₂	N ₂	He
	Per Cent by Volume					
Model Dome, Las Animas Co., Colo., U.S.A....	0 00	0 00	12.19	0.92	79.71	7.18
Pondera field, Pondera Co., Mont., U.S.A. ...	65 60	31.04	0 90	0.07	2 14	0 25
Cliffside field, Potter Co., Tex., U.S.A....	59 80	13 70	0.70	0.10	23.90	1 80
Foremost field, Alberta, Canada	90 90	0 60	0 00	0.00	8 50	0 22
Walden field, Jackson Co., Colo., U.S.A. . .	0 52	3 95	92.14	0 09	3 16	0.14
Woodside anticline, Emery Co., Utah, U.S.A.	0 00	5.70	31 70	0.27	61.02	1.31
McKittrick field, Kern Co., Calif., U.S.A. . .	66 20	1 00	30 40	0 00	2 40	
Buena Vista Hills, Kern Co., Calif., U.S.A. . .	42 20	37 50	16 50	0 00	3 80	

TABLE 8.12
COMPOSITION OF MINE GASES

SOURCE	HYDRO-CARBONS	CO ₂	O ₂	N ₂	He	A
	Per Cent by Volume					
Metal mine, Cripple Creek, Colo., U.S.A		18 00	0 30—	81 00		
Coal mine, Anzin, France	97 92	0 16		1 85	0.044*	0 021†

* Traces of Ne.

† Traces of Kr and Xe.

bon-oxidizing bacteria or their fossil remains as very sensitive indicators of traces of hydrocarbons (e.g., ethane) in soil forms the basis of the geomicrobiological prospecting for petroleum. Another method is based on the detection of characteristic disturbances in the growth of plants, caused by the emanation of small amounts of ethylene and its homologues found in petroleum (v. Thyssen-Bornemisza, 1943).

The gases in metal mines contain nitrogen, carbon dioxide, and oxygen. Some mine gases are almost pure nitrogen, and the content of oxygen may be less than 1 per cent.

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Gases from many mineral springs are relatively high in nitrogen and helium; the content of helium may be more than 10 per cent. These gases occur also in the firedamp of coal mines, in gas collected from a salt mine near Stassfurt in Germany, and in fumarole gases. The gases of hot springs and fumaroles are commonly high in CO_2 . In fumaroles, hot springs, and mineral springs the presence of carbon dioxide is probably due to volcanic and chemical activity.

Analyses of two mine gases are given in Table 8.12. They are quoted from Dobbin (1935) and Rogers (1921), respectively. Analyses of gases of volcanic origin were given in chapter 5.

BIOGEOCHEMISTRY OF THE SEA

The biosphere and the hydrosphere are closely connected with each other because water is essential for all life. It forms 80 per cent or more by weight of the protoplasm. The marine biocycle is the most important part of the biosphere.

The activities of the plants in the sea are restricted to the upper layers, called the euphotic zone. In near-shore waters the thickness of this zone is only some meters, but in the open ocean, where the transparency of water is higher, this zone may attain a thickness of several hundred meters. Sea water is a plant nutrient containing everything essential for the growth of algae. Dissolved phosphate and nitrate are, however, the factors limiting the occurrence of plant life in the euphotic zone. The quantity of these salts consequently affects animal life in the sea as well. The distribution of animals is also governed by the salinity of the water. The role of phosphates and nitrates in the cycle of life in the sea is presented in Figure 8.6, according to Harvey (1928).

Sea water contains a ready supply of carbon dioxide, which may fluctuate, within reasonable limits, without a material change in the hydrogen-ion concentration. The phytoplankton organisms, which form the plant life of the open ocean, absorb carbon dioxide from sea water and release oxygen. They also absorb inorganic compounds of phosphorus and nitrogen, which are used for the synthesis of organic matter. However, the ammonium released by the decomposition of the dead organisms is not utilized as such by phytoplankton. It is first converted into nitrate. The phytoplankton organisms are, further, able to remove silver, gold, and other heavy metals from sea water by adsorption on their surface.

Plants are the most important consumers of inorganic matter in

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the sea. They form the supply of food necessary for the existence of animal life, viz., zooplankton and marine animals, in the sea. The animals, in turn, excrete carbon dioxide, ammonia, phosphates, and soluble organic substances. Ions are adsorbed from sea water on their surface, and certain species enrich elements, e.g., vanadium, strontium, copper, and bromine, in their cells.

The growth and decomposition of marine organisms produce changes in the chemical composition of sea water. Practically all substances extracted by the organisms return to solution by metabolic processes or during their decay. However, a small fraction of organic

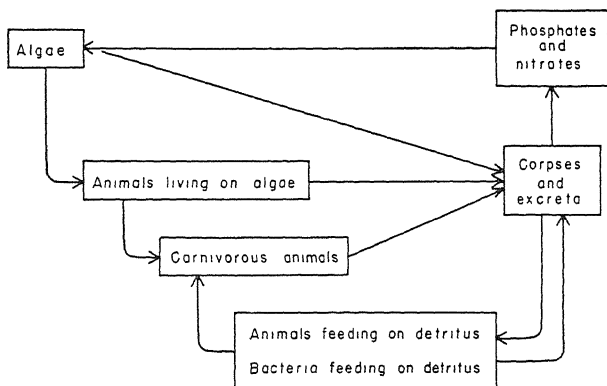


FIG. 8.6.—Phosphates and nitrates in the cycle of life in the sea. (Based on material from *Biological Chemistry and Physics of Sea Water*, by H. W. Harvey, 1928. Courtesy of Cambridge University Press.)

matter is accumulated in marine sediments and is consequently lost to the cycle; but some of it is later released by benthic organisms participating in chemical processes in the sea.

The different elements found in sea water are concentrated at different rates in marine organisms. If their concentration therein is compared with that in sea water, concentration factors may be calculated. The highest factors belong to nitrogen and phosphorus, which limit organic activity in the sea; but the concentration of carbon, silicon, fluorine, iron, and copper may also be considerably affected by biological activity.

Marine animals are readily permeated by the water molecules and the ions in sea water. Actually, the blood and body fluids of many species are in osmotic equilibrium with sea water. The lower fresh-water animals do not possess this property. Sea water and the body fluids of marine invertebrates contain salts in nearly identical propor-

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tions. This similarity, in a modified form, is present also in fresh-water and terrestrial animals. With reference to the major inorganic constituents, the body fluids correspond to a somewhat altered sea water. The analyses presented in Table 8.13, which is quoted from Sverdrup, Johnson, and Fleming (1942; recalculated from Robertson, 1939), illustrate this similarity.

THE ANTHROPOSPHERE

The Russian geologist, A. P. Pavlov (1854-1929), introduced the concept of the anthropogenic era into geology, emphasizing the fact that man is becoming a mighty and ever growing geological force, in spite of the insignificant mass of mankind on the Earth. Man has

TABLE 8.13
RELATIVE CHEMICAL COMPOSITION OF BODY FLUIDS OF
SOME MARINE ANIMALS, ADJUSTED TO Na = 100*

Element	Sea Water	<i>Echinus esculentus</i>	<i>Homarus vulgaris</i>
Cl	180	182	156
Na.. . . .	100	100	100
Mg	12 1	12 0	1 5
S in SO ₄ ...	8 4	8 5	2 2
Ca... . .	3 8	3 9	5 0
K.	3 6	3 7	4 7

* Based on material from *The Oceans*, by H. U. Sverdrup, M. W. Johnson, and R. H. Fleming. Copyright 1942 by Prentice-Hall, Inc. Used by permission.

thus created a new part of the biosphere, which is chemically highly active. This subdivision of the biosphere is called the anthroposphere. Vernadsky (1945) introduced the name no-osphere for the same purpose.

Although the geological age of man is around 100,000 years, man as a geochemical agent has been active only during the last 10,000 years. Geochemically, the anthroposphere is of constantly increasing interest and importance. Man is causing changes in the geochemical cycles of the elements and disturbing their natural balance in the uppermost geospheres. Iron, which as a mineral is a curiosity, is now being produced at an annual rate in excess of 10^8 tons. Some metals, like the alkali and alkaline-earth metals, aluminum, and magnesium, which never existed in the native state in Nature, are produced in constantly increasing quantities. Similarly, the amount of artificial inorganic and organic compounds, minerals, and rocks produced in

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the anthroposphere is continually growing. Elements and their compounds are extracted from the hydrosphere (sodium chloride, magnesium, iodine, etc.) and from the atmosphere (nitrogen as a source of nitrates and ammonia) which consequently are new, important sources of raw materials. Many chemical processes in the biosphere are controlled, and directed courses are assigned to them. Man tends to increase the area and mass of the biosphere in order to acquire new living space and more food. Geochemically very interesting is the continual concentration of the noble metals in the anthroposphere. In addition, other metals have been transported from the lithosphere to the anthroposphere, e.g., radium. The new artificial long-lived radioactive elements, neptunium and plutonium, exist predominantly in the anthroposphere. Their abundance should be definitively the best-known among all elements in the Periodic Table.

The geochemical cycle of carbon, of all elements, is the one which is most strongly influenced by the industrial activity taking place in the anthroposphere. The role of human activity in modifying the cycle of carbon is discussed in chapter 19.

COSMOCHEMISTRY AND GEOCHEMISTRY

SCOPE OF COSMOCHEMISTRY

THE name cosmochemistry was suggested (Wildt, 1940*b*) to designate the branch of science which deals with the constitution and evolution of matter under all cosmic conditions with special reference to the chemistry of cosmic phenomena. Chemistry is here understood in the widest possible sense, as the science of matter in all its manifestations. According to this definition, cosmochemistry is the natural end-product of geochemistry, expanded and applied to the planets, which it covers as planetary chemistry, and then to the chemical problems of the Universe. Geochemistry may be considered a special branch of planetary chemistry.

The chemical study of the meteorites referred to in chapter 1 is an important connecting link between cosmochemistry and geochemistry. The first contact between astronomy and chemistry was created when the cosmic origin of the meteorites was understood and when spectrochemical analysis was first applied to stellar problems.

Early trends in cosmochemical speculation are represented by the ideas of Nicholas Cardinal of Cusa (Nikolaus von Kues, 1401–64) and Leonardo da Vinci (1452–1519). They believed in the identity of terrestrial and cosmic matter. Later, Robert Boyle, Christian Huygens, and Isaac Newton were convinced of the uniform character of matter throughout the Universe.

It was shown in chapter 2 that, as far as information is available, the qualitative composition of matter is identical and its quantitative composition tends to be similar in all parts of the Universe, if such local differences are left out of consideration as are caused by processes already at least partly understood, such as the differentiation in the Earth's lithosphere.

The study of the chemical composition and chemical evolution of

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the Earth is one of the cardinal tasks of geochemistry. In this research the results of modern cosmochemical investigations are helpful, partly because of the role of geochemistry as a chapter in the universal planetary chemistry and partly because of the close connections existing between nuclear physics and chemistry, on the one hand, and astrophysics, on the other. The meteorites, which represent a special class of cosmic material because they are directly available for research, have given much information of definite importance pertinent to the chemical composition and chemical evolution of the Earth (see chaps. 1 and 3). Additional information is obtained from the study dealing with comets and meteors, the constitution and composition of the planets and their atmospheres, the composition of the Sun and of other stars, and the composition of interstellar matter. Although none of these subjects actually belongs to the domain of geochemistry, short accounts of those not previously discussed will be presented in the following pages because they furnish important points of comparison for the problem investigated and further elucidate the distribution of matter and the abundance of elements in the Solar System and in the Universe.

COMETS AND METEORS

The nuclei of the comets probably consist of a swarm of solid particles of meteoric matter, even though a sizable body within the nuclei never has been observed. The only clues concerning the composition of the comets are obtained from their spectra. When they are closest to the Sun, they produce a coma consisting of dust and a number of gases surrounding the heads or the nuclei. Compared with the temperatures of stellar atmospheres, the temperatures of the cometary atmospheres are very low.

The elements which compose the cometary gases are the same that are abundant elsewhere in the Universe. Carbon is the principal element, followed in importance by hydrogen, nitrogen, and oxygen. According to Swings (1943), the following molecules have been identified in the spectra of comets: OH, NH, CN, CH, C₂, CH⁺, CH₂, CO⁺, N₂⁺, and probably NH₂ and OH⁺. The molecules CH, CH₂, and NH₂ are concentrated near the nucleus, whereas the range of OH, NH, CN, and C₂ is wider and the ionized molecules CH⁺, CO⁺, and N₂⁺ extend into the tail but are also observed in the head, close to the nucleus. At small heliocentric distances (within the orbit of Venus) the most sensitive lines of sodium appear in addition, both in the

head and in the tail, and the spectrum of the great comet 1882II also showed the presence of iron and possibly chromium and nickel. So far, CH_2 is the only polyatomic molecule identified in comets. Nothing is known about the abundance of molecules in the comets.

When the comets travel far from the Sun, CN causes their principal radiation. At smaller distances from the Sun, C_2 and CH in the spectra increase in intensity. Within the orbit of Mars, CO and N_2 appear in the spectrum, chiefly in the radiation coming from the tail.

The radicals OH, CH, CN, etc., are chemically unstable. Their presence in the low-temperature cometary atmospheres is due to the low density of these atmospheres, which results in the almost total absence of collisions between the molecules and other particles. In like manner, CH, CN, and CH^+ are observed in the interstellar gas, which also is of a very low density (see under "Interstellar Matter," p. 381). The similarity in constitution between cometary and interstellar gases is caused by the remarkable constancy of the cosmic abundance of the elements and by the characteristic physical properties of the molecules (Swings, 1943).

The chemically unsaturated radicals are formed by the photodissociation or photoionization of more complex parent-molecules which are chemically stable and occur in the cometary nuclei as occluded gases. The parent-molecules are liberated by the action of solar radiation. Swings (1943) suggests that a part of the stable molecules must be polyatomic compounds of hydrogen, carbon, nitrogen, oxygen, and sulfur, and possibly of some other elements. Therefore, e.g., the NH molecules must originate in the photodissociation of stable molecules, probably ammonia, set free from the solid constituents of the comet. It is known that the volume of gases released by meteorites upon heating may be as high as sixty times the volume of the heated material. According to Merrill (1926), carbon dioxide, hydrogen, and carbon monoxide are the most abundant gaseous constituents of the stones, and hydrogen, carbon monoxide, and nitrogen the most abundant gases occluded in the irons. Methane, sulfur dioxide, and hydrogen sulfide are also met in the meteorites. It is probable that these gases are present in the comets and that water vapor and ammonia are also found therein.

The ultimate chemical composition of cometary matter is still unknown, but it is supposed that the comets are genetically related to meteorites and resemble them rather closely.

It is believed that each meteor stream has its origin in a comet.

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There are two kinds of meteors, viz., the shower meteors and the sporadic meteors. The shower meteors contain calcium, and they are believed to be stony particles. Calcium is absent in other meteors. Along with calcium, the following elements have been detected, by spectrochemical analysis, in the meteors: sodium, magnesium, aluminum, silicon, chromium, manganese, and nickel.

INTERNAL CONSTITUTION OF THE PLANETS

The planets are usually divided into the groups of the terrestrial and giant (major) planets, which are separated in space by the group of the asteroids or the minor planets. The group of the Earth-like planets consists of Mercury, Venus, Earth, Moon, and Mars. These planets have small masses, not exceeding the mass of the Earth, and mean densities higher than the density of the upper lithosphere. They are close neighbors of the Sun. Pluto, the outermost planet in the Solar System, also belongs to the group of the terrestrial planets by its physical properties. The major planets, Jupiter, Saturn, Uranus, and Neptune, differ strikingly from the terrestrial planets. Their masses are very large, and their average density is only 25–50 per cent of that of the upper lithosphere. Their orbits are located in the outer regions of the Solar System.

The current hypothesis of the structure of the Earth's interior has furnished the pattern for the interpretation of the internal structure of the other planets. The structure of the terrestrial planets differs materially from that of the giant planets. According to Jeffreys (1937), Venus, like Earth, has an iron core with a radius of about half the planetary radius. In Mars the radius of the iron core is much smaller than in the Earth, possibly 42 per cent of the planetary radius, and Mercury and the Moon have no iron core at all but consist entirely of silicates. This is shown by their low density; the density values are presented in Table 9.1 according to Wildt (1939a). However, Jeffreys thinks that Mercury might possess a very small core, with a radius of approximately 30 per cent of the total radius; but this conclusion is uncertain because there is little hope that the mass of Mercury will ever be accurately known.

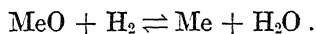
The giant planets are believed to have a very similar internal constitution. Their masses are far more concentrated toward the center than are the masses of the terrestrial planets. Their surface layers consist of a very light material. Jeffreys (1924) suggested that Jupiter and Saturn have a rocky core with a density of about 3, surrounded

by a thick layer of solid ice and carbon dioxide (density about 1), which is covered by a deep atmosphere. Wildt (1934*b*, 1938) constructed a three-shell model for the giant planets, which consists of a dense core, similar in structure to the terrestrial planets, surrounded by a vast layer of ice, several thousand kilometers in thickness. On top of the ice layer there is an envelope of highly compressed solid gases, mainly hydrogen, but also helium, neon, nitrogen, and carbon dioxide. This model is based on geochemical reasoning because it is supposed that the giant planets were formed from solar material without any considerable loss of volatile constituents, as the large masses of the giant planets and their low rates of loss of the atmospheric constituents suggest. An excess of the lighter elements, espe-

TABLE 9.1
AVERAGE DENSITY OF THE PLANETS

Planet	Average Density ($\text{g}\cdot\text{cm}^{-3}$)
Mercury	2.86
Venus	4.86
Earth	5.52
Moon	3.33
Mars	3.84
Jupiter	1.30
Saturn	0.69
Uranus	1.10
Neptune	1.62

cially hydrogen, is supposed to have been present in the primordial atmospheres of the giant planets. Oxidation of the metals and the subsequent formation of water vapor were the main chemical processes taking place during the early stages of the cooling of these bodies. The great excess of hydrogen was responsible for the formation of a metallic core:



The oxides of iron, in particular, are reduced by hydrogen at high temperatures, and therefore iron would mainly collect in the core. On the other hand, the oxides of silicon and of the principal metallic constituents of igneous rocks other than iron are not reduced by hydrogen, and therefore they would form silicates similar to the terrestrial silicate minerals (Russell, 1935). Consequently, the early condensates formed a metal phase and a silicate phase, which were separated under the influence of gravity (Tammann, 1931). They formed the core of the giant planets. Their protoatmospheres consisted chiefly of hydrogen and water vapor. On further cooling, the water vapor

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settled on top of the silicate mantle as a layer of ice, and hydrogen and other gases followed during the progressive cooling of the planet. The condensation of water vapor and hydrogen may have taken place directly from the gaseous state without passing through the liquid phase, and therefore the giant planets may never have possessed a hydrosphere containing the bulk of water, even though a shallow layer of water might have been present. The reactions taking place in the cooling atmospheres of the giant planets will be discussed in the coming paragraph.

It seems to be possible that the primeval giant planets, perhaps, were not rich enough in oxygen to allow the formation of a thick ice layer, because oxygen combined preferentially with silicon and the metals due to the higher energy of formation of their oxides as com-

TABLE 9.2
DENSITY LIMITS IN TWO-SHELL MODELS
OF THE GIANT PLANETS

Planet	Density of Shell ($\text{g} \cdot \text{cm}^{-3}$)	Density of Core ($\text{g} \cdot \text{cm}^{-3}$)
Jupiter	≥ 0.78	≥ 2.80
Saturn	≥ 0.425	≥ 1.48
Uranus	≥ 0.66	≥ 3.36
Neptune	≥ 0.96	≥ 3.44

pared with the energy of formation of water. Therefore, Wildt (1947) deduced two-shell models for the giant planets, in which the core has a density of the order of the mean density of the Earth, or a little higher, owing to the higher pressure inside the giant planets. Theoretical calculations showed that the density of the shell must be very low, and therefore the only constituent of the shell may be the permanent gases in a highly compressed state or even solidified. The density limits of the two-shell models are presented in Table 9.2 according to Wildt (1947).

The outer shell occupies more than 80 per cent of the volume of the planets. The best observational evidence of the fluidity of the outer shell on Jupiter is the movement of the Red Spot which Peek (1940) has analyzed. Wildt (1939b) suggested that the Red Spot may be a solid body floating in an "ocean" of permanent gases. Wasiutyński (1946) concluded that the outer layer of Jupiter, down to a depth of the order of 10,000 km, is fluid and that a similar outer layer, probably still thicker, seems to exist on Saturn.

Very little is known of the physical character of the asteroids. The variability of the light reflected by some of them has tentatively been ascribed to their nonspherical shape. Even the largest asteroids cannot retain an atmosphere. Most of the satellites of the giant planets appear to be like the Moon in their internal constitution, but some of them which have mean densities less than $1 \text{ g} \cdot \text{cm}^{-3}$ are presumably similar to the outer layer of the giant planets.

The amount of precise information so far available on the chemistry of most of the planets is very small. Therefore, one must conclude that the planetary models are still tentative. However, with reference to the bulk chemical composition, the giant planets evidently are characterized by the high abundance of hydrogen, a conclusion deduced from the existence of vast amounts of methane and ammonia in their atmospheres. The presence of ammonia also suggests a considerable abundance of nitrogen.

PLANETARY ATMOSPHERES

In its beginning, the chemical evolution of the cooling planets was governed by the laws of thermochemical equilibrium. When the surfaces of the planets had cooled down sufficiently, a number of photochemical reactions probably took place, very likely gaining in prominence in the course of time. The energy required by these reactions was furnished by the ultraviolet radiation of the Sun.

All polyatomic molecules in the planetary atmospheres are sensitive to ultraviolet radiation. Highly susceptible molecules are O_3 , CO_2 , NH_3 , CH_4 , and others. To maintain the observed stationary composition of the atmospheres, the photochemical decomposition must be followed by secondary chemical reactions by which the products formed by dissociation are reunited.

It is generally assumed that the surface temperature of the planets was once very high. Under such circumstances, only the planets with the highest masses could retain the constituents of their protoatmospheres. The small planets lost their entire atmospheres into interplanetary space. The terrestrial planets with the greater masses lost their light material and were able to retain only very small quantities of the gases which are now found among the constituents of their atmospheres. This is the cause of their present deficiency in hydrogen and its compounds with carbon and nitrogen. In like manner, helium has been lost from their atmospheres, along with other light gases, such as neon. Nitrogen was lost because it was dissociated into atoms

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(Wildt, 1934*b*). Oxygen was retained in combination with other elements; free oxygen would escape.

The present atmospheres of such terrestrial planets as have been and still are massive enough to retain them consist almost exclusively of elements not lighter than oxygen. It seems to be probable that their atmospheres are of secondary origin, being produced by compounds dissolved in the silicate melts of their lithospheres. During the formation of a solid crust, these gases escaped, and additional amounts of them were produced during the weathering of the crust of some of the terrestrial planets and by volcanic activity.

Also the giant planets may have lost a large part of the lighter gases in their original gaseous envelopes, but they were able to retain large quantities of their primordial atmospheric constituents. Their atmospheres evidently are devoid of oxygen and its compounds but contain hydrogen and its compounds. The prevalence of hydrogen in their atmospheres may be understood as the result of an enormous supply of hydrogen. Helium may also be abundant.

The discussion presented above shows that there is a correlation between the mass of the planets and the mass and composition of their atmospheres. Those of the terrestrial planets contain oxides, whereas hydrides abound in the atmospheres of the giant planets.

No free halogen molecules exist as permanent constituents of planetary atmospheres because the halogens are chemically highly active. Molecular hydrogen and nitrogen are well shielded against decomposition by the presence of polyatomic molecules, which absorb the ultraviolet radiation.

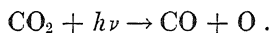
THE TERRESTRIAL PLANETS

Mercury probably does not possess any atmosphere, a fact due partly to its small mass and partly to its high surface temperature. There is some evidence that Mercury has not yet entirely lost its atmosphere (Phillips, 1936), but any possible atmosphere must be very thin.

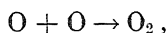
The atmosphere of Venus is deep and probably extends for several kilometers above the visible surface of clouds surrounding the planet. It is probable that the atmosphere consists almost exclusively of carbon dioxide, which was identified therein by Adams and Dunham (Adams, 1932). There are hundreds of times more carbon dioxide in the atmosphere of Venus than in that of the Earth. No evidence for the presence of water vapor or oxygen has been found in the atmos-

phere of Venus above the cloud layer. Wildt (1942a) suggests that less water was originally available on Venus than on the Earth. Practically all water on Venus may have been bound in hydrated minerals, and a hydrosphere never existed. However, the presence of traces of water vapor cannot be ruled out at present. St. John and Nicholson (1922) calculated that the amounts of oxygen and water vapor must be less than 1 m-atm and less than 1 mm-atm, respectively. In other words, the amount of oxygen is less than one-thousandth and the amount of water vapor less than one-tenth of the corresponding quantities of these gases in the terrestrial atmosphere. Independent spectroscopic evidence of the scarcity of oxygen on Venus was presented by Wildt (1940a), according to whom the lack of oxygen in the atmosphere of Venus indicates that its protoatmosphere must have been extremely poor in water vapor, if Tammann's (1924b) theory of the origin of terrestrial oxygen is accepted (see chap. 27). In the present atmosphere the partial pressure of water vapor must be far below that required for saturation and condensation.

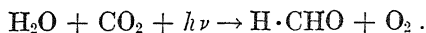
Because oxygen is practically absent, the main photochemical reaction believed to take place in the atmosphere of Venus is (Wildt, 1937):



The most important secondary reaction would be the partial recombination:



which would be followed by the rapid photochemical dissociation of the oxygen molecules. Finally, carbon monoxide would be reoxidized to dioxide. Wildt further suggested that the oxygen originally present in the atmosphere or formed by thermal dissociation therein was consumed in the oxidation of silicates, leaving a tenuous atmosphere of water vapor. Because a protective oxygen or ozone screen is absent in the atmosphere of Venus, it might be possible that some formaldehyde is produced in the reaction:



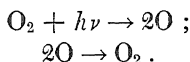
However, no evidence for the presence of formaldehyde has been found in the ultraviolet spectrum of Venus, and therefore the clouds surrounding the planet cannot be composed of solid polyoxymethylene hydrates (Wildt, 1942a); their nature still is unknown.

The chemical composition of the Earth's atmosphere was discussed

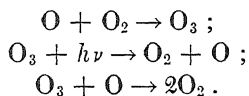
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in chapter 7. It is calculated to amount to 8,000 m-atm. The atmosphere of the Earth, like that of Venus, is predominantly turbid.

The ozone equilibrium in the terrestrial atmosphere was explained by Wulf and Deming (1936). The oxygen molecules are decomposed photochemically and may yield both unexcited and excited atoms, depending on the wave length of the radiation. At great altitudes the following reactions take place:



At lower altitudes the reactions are:



The condition necessary for the formation of ozone is the presence of notable amounts of free oxygen in the atmosphere. Wulf and Deming (1936) consider that ozone is maintained in a photochemical steady state by solar radiation, which is absorbed by oxygen and ozone. They think that the three last-mentioned reactions essentially govern the ozone in the atmosphere.

The Moon must be regarded as a twin planet rather than as a satellite. According to V. G. Fessenkoff (see Struve, 1944; Herzberg, 1946), the mass of a vertical column of unit cross-section in the lunar atmosphere is less than a millionth of the corresponding mass in the Earth's atmosphere. Herzberg (1946) assumes that the composition of the Moon's atmosphere is similar to the atmosphere of the head of a comet, owing to the accretion of meteorites on the lunar surface.

The escape velocity on Mars is high enough to retain water vapor and all heavier gases but not hydrogen and the other light gases. However, very much less water vapor must be present in the Martian atmosphere than in the Earth's atmosphere, even though evanescent white cloud formations and areas partially concealed by haze have been observed. Hess (1948) found, from meteorological considerations, that a total water-vapor content of about 0.5 mm in the Martian atmosphere is sufficient to account for the presence of the clouds. The height of the clouds, according to Adel and Slipher (1934c), is more than 20 km, but the pressure on the surface of Mars probably is only a small fraction of the pressure on the Earth's surface, and therefore the atmosphere of Mars is rarer than the atmosphere of the Earth. According to Hess, the mass of the Martian atmosphere is

some 20 per cent of the mass of the terrestrial atmosphere. The Martian atmosphere is estimated to be about 100 km deep.

Kuiper (1947) found that the Martian atmosphere contains slightly more carbon dioxide than does the atmosphere of the Earth. The content of methane, ammonia, and nitrous oxide is zero or negligible. The bulk of the Martian atmosphere may consist of nitrogen. The Martian polar caps very probably consist of a thin layer of frozen water, because the temperature is too high to permit the presence of solid carbon dioxide.

The existence of oxygen in the atmosphere of Mars is still unproved. Adams and Dunham (1934) estimated that the amount of oxygen, in any case, must be less than 0.1 per cent of the amount of oxygen in the terrestrial atmosphere. However, it is possible that the atmosphere of Mars once contained free oxygen or ozone, which was consumed in the oxidation of iron; hence the red color of vast areas of the surface of the planet. Consequently, almost all the Martian oxygen is now fossil oxygen (see chap. 27). With the exception of the Earth, no other planet is known to contain oxygen or ozone in amounts detectable by the spectrograph. If the oxygen content is very low, approximately $5 \text{ g} \cdot \text{cm}^{-2}$, the ozone layer is formed close to the surface of the planet, being able to attack the crust chemically. Wildt (1934a) believes that this actually happened on Mars during an earlier stage in its evolution. The great scarcity of oxygen agrees well with the scarcity of water on the planet. According to Wildt (1942b), the loss of water vapor from the atmosphere of Mars has been appreciable during the whole period of solidification of its silicate crust.

Comparative data dealing with the composition of the atmospheres of Venus, Earth, and Mars are presented in Table 9.3, which is quoted from Wildt (1942). Fossil oxygen and carbon dioxide and water vapor bound in the sediments are also considered among the data pertaining to the Earth.

Pluto probably has no atmosphere at all, because it is only slightly larger than Mercury and because its surface temperature lies near absolute zero. However, the presence of a very thin methane atmosphere is not wholly excluded (Kuiper, 1944).

THE GIANT PLANETS

In contrast with the terrestrial planets, the giant planets with low surface temperatures have very deep atmospheres. The compressi-

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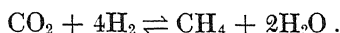
bility and viscosity of their atmospheres approach that of common liquids (Wildt, 1938), and at lower levels their atmospheres probably would resemble the terrestrial hydrosphere rather than an atmosphere.

Because of their large masses, the giant planets have been able to retain most, if not all, of the original constituents of their atmospheres, including, also, much of the hydrogen and helium originally present. In their present composition their atmospheres are characterized by the abundance of hydrogen compounds. Their protoatmospheres probably consisted of hydrogen, helium, nitrogen, carbon dioxide, and small amounts of other inert gases, and some compounds

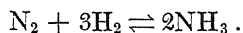
TABLE 9.3
PARTIAL CHEMICAL COMPOSITION OF THE ATMOSPHERES
OF VENUS, EARTH, AND MARS

CONSTITUENT	VENUS	EARTH, SUM TOTAL	EARTH, PRESENT ATMOSPHERE	MARS
	g · cm ⁻²			
Oxygen	<2	490-780	230	<2
Carbon dioxide . . .	40-80	7,300-9,700	0.4	<20
Water vapor. . .	<0.1	289,000	variable	<0.05

of the halogens and of sulfur. According to Russell (1935), carbon dioxide reacted with hydrogen to produce methane and water vapor:



At temperatures below 300° C., practically all carbon dioxide was converted into methane. Nitrogen reacted with hydrogen to produce ammonia at low temperatures and pressures:



The oxides of nitrogen are endothermic and therefore would tend to dissociate rather than form.

At a temperature of approximately 1,000° C. the atmosphere of a giant planet would consist mainly of hydrogen, water vapor, nitrogen, and carbon dioxide. Any carbon monoxide originally present would have been completely oxidized to dioxide. When the temperature falls, carbon dioxide is converted into methane before water

vapor reaches its critical temperature and begins to condense. When most of the water vapor has been precipitated, nitrogen is converted into ammonia. The oxides of iron act as catalysts, at least in the formation of methane, and electrical discharges in the atmosphere activate the formation of ammonia.

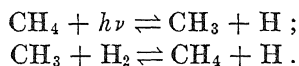
When the temperature has fallen to the present terrestrial level, there exists an extensive atmosphere consisting of hydrogen, methane, ammonia, water vapor, and inert gases, but of only little or no nitrogen and carbon dioxide. The hydrosphere contains ammonia and dissolved sulfur and halogen compounds. Upon further cooling, water vapor will freeze out, and the monohydrate $\text{NH}_3 \cdot \text{H}_2\text{O}$ will probably form in the hydrosphere. Upon the freezing of the hydrosphere, which probably contained only little dissolved salts, ammonia will evaporate into the atmosphere, according to Tammann and Rocha (1932). Therefore, the bulk of the ammonia and all the methane still remain in the atmosphere.

Methane and ammonia, as a matter of fact, are the only gases so far identified in the atmospheres of the giant planets. There probably is no water vapor, ozone, carbon oxides, and hydrogen sulfide in the visible layer of their atmospheres because these gases actually have been frozen out. The presence of methane, the major constituent, was established by Wildt (1932*a, b*) and by Adel and Slipher (1934*b*). The presence of ammonia in the atmospheres of Jupiter and Saturn was demonstrated by Wildt (1932*a*) and definitely proved by Dunham (1933). It seems to be necessary to assume that the atmospheres also contain a large excess of molecular hydrogen and a certain amount of molecular nitrogen. The presence of these molecules is difficult to establish by spectrochemical analysis, though not impossible (Herzberg, 1938). Moreover, the formation of methane during the cooling of the primeval atmosphere rich in hydrogen and the oxides of carbon implies, according to Russell (1935), the simultaneous synthesis of higher hydrocarbons; but the fact that none of these is now present affords indirect proof of the existence of much hydrogen in the atmospheres of the giant planets. The higher hydrocarbons are likely to be decomposed photochemically and because of the action of free hydrogen. The painstaking studies of Adel and Slipher (1943*b, c*) failed to establish the presence of appreciable quantities of ethane, ethylene, and acetylene, the only hydrocarbons which need to be considered because they have boiling points low enough to allow them to be present as atmospheric constituents of the very cold giant planets.

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However, Adel and Slipher believe that these hydrocarbons and many others exist below the atmospheres of the major planets. Adel and Slipher (1934a) also find a reasonable explanation of the prominence of methane in the fact that, at the extremely low temperatures in question, the vapor pressure of methane is very much in excess of the vapor pressure of any other hydrocarbon likely to exist in the atmosphere. Because methane and ammonia are compounds saturated with hydrogen and because they are very stable, the conclusion follows that collision reactions may have continued in the atmospheres of the giant planets over long periods of time, finally leading to the formation of atmospheric constituents of maximum stability with reference to the physical conditions which prevail in the atmospheres of these planets.

Wildt (1937) has given a photochemical explanation of why the number of the atmospheric constituents of the giant planets is so small. The reason is that all polyatomic molecules observed in the spectra of these planets are readily decomposed by the ultraviolet radiation of the Sun. With reference to methane, the fundamental reactions would be:



Therefore, a large supply of hydrogen would be required for this reaction, and, according to the theory, this supply actually is available. However, to Bobrovnikoff (1944) the postulated abundance of hydrogen appears questionable in view of the existence of Titan's atmosphere. Titan is able to retain methane but not free hydrogen.

According to Wildt (1937), ammonia also should decompose photochemically in the atmospheres of Jupiter and Saturn:



but secondary reactions reproduce ammonia at a considerable rate. Other photochemical reactions possible in planetary atmospheres should remove carbon monoxide, carbon dioxide, and hydrogen sulfide from the atmospheres of Jupiter and Saturn.

The atmosphere of Jupiter is very deep, but its depth is negligible compared with the radius of the planet. According to Adel and Slipher (1935), the amount of methane in the absorbing layer is about 800 m-atm, which corresponds to a total of $8 \cdot 10^{16}$ tons of methane in the whole absorbing layer of Jupiter. The bulk of ammonia is fro-

zen. Dunham (1939a) estimates the amount of ammonia above the reflecting layer in the atmosphere as about 10 m-atm.

The composition of the Saturnian atmosphere corresponds to that of the Jovian atmosphere. However, the surface temperature of Saturn is lower, and consequently there is more methane and less ammonia present in the Saturnian atmosphere, because more ammonia is frozen out. According to Adel and Slipher (1935), the quantity of methane in the absorbing layer of the Saturnian atmosphere is greater than 800 m-atm, and therefore the total in the absorbing layer will be about $6 \cdot 10^{16}$ tons.

Titan, Saturn's largest satellite, has an atmosphere of a composition similar to Saturn's (Kuiper, 1944). However, its optical thickness is somewhat less. No other satellite has been found to possess an atmosphere.

Methane is the only atmospheric constituent of Uranus. Adel and Slipher (1935) estimate its amount in the absorbing layer of the atmosphere of Uranus as 6,400 m-atm, corresponding to a total of more than $8 \cdot 10^{16}$ tons. The methane bands are stronger in the spectra of the outer planets, probably because ammonia has been frozen out and thus one sees deeper. Ammonia bands are absent in the spectrum of Uranus.

The atmosphere of Neptune is known to contain only methane, and the absence of ammonia bands in the spectrum of this planet shows that ammonia has been completely frozen out. At the very low surface temperature of Neptune, methane must be on the verge of condensation. The amount of methane in the absorbing layer is 40,200 m-atm, corresponding to a mass of $60 \cdot 10^{16}$ tons in the whole absorbing layer of the atmosphere (Adel and Slipher, 1935).

INTERSTELLAR MATTER

Solid inorganic matter is distributed throughout the whole Universe. Interstellar space contains at least three forms of obscuring solid matter, viz., interstellar smoke, cold bodies, and dark stars. The dark stars are believed to be small stars which give off little or no visible radiation. The cold bodies are small masses which may reach several tons in weight. The interstellar smoke often forms extensive cosmic clouds.

Interstellar space also contains interstellar or cosmic gas, which consists of molecules, free atoms, and electrons. It is held probable that interstellar solid particles (smoke) are formed by condensation

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from the interstellar gas, starting with the formation of CH^+ molecules from C^+ and H and CH from C and H and followed by the capture of a second H atom and by that of other atoms (ter Haar, 1943, 1944; Kramers and ter Haar, 1946). The smoke formation is consequently an agglomeration of atoms, and the formation of diatomic and probably triatomic molecules is the first step of this coagulation. The particles are destroyed by dissociation and by mutual collision. Consequently, an equilibrium between the gas and the solid particles is reached.

The average density of stellar matter, spread over the entire volume of the Galaxy is only about $10^{-28} \text{ g}\cdot\text{cm}^{-3}$. The upper limit of the density of all interstellar matter, established from dynamical considerations, is $3\cdot 10^{-24} \text{ g}\cdot\text{cm}^{-3}$ (the Oort limit). The mean density of cosmic smoke is approximately $10^{-26} \text{ g}\cdot\text{cm}^{-3}$. Although the interstellar gas contains only a few thousand molecules in a cubic meter, the dimensions of the Galaxy are so vast that the mass of the interstellar gas is not negligible. The mass of the interstellar gas and the smoke particles therein are of the same order of magnitude as the mass of the stars. According to Adams (1941), the volume of interstellar smoke and gas may be several times as high as the volume of all visible matter so far discovered in space.

The following neutral and ionized elements so far have been detected, by their absorption spectra, in the interstellar space: Na , Ca , K , Fe , Ti^+ , and Ca^+ . The following diatomic molecules are present: CN , CH , CH^+ , and perhaps NaH . Emission lines of hydrogen, nitrogen, and oxygen have also been observed in the spectra of certain interstellar regions where the density of gas is comparatively high. The shielding effect of the Lyman continuum of atomic hydrogen largely prevents the ionization of nitrogen and oxygen. Moreover, the ionization of hydrogen may prevent the formation of the CH , NH , and OH molecules, which consequently may be more numerous in the un-ionized regions of the space. Hydrogen presumably is the main source of interstellar electrons, but at any considerable distance from the high-temperature stars and from clusters of such stars the electrons must come from carbon, sulfur, chlorine, and the metals. It is likely that in the regions of un-ionized hydrogen most of the free electrons are furnished by carbon (Strömgren, 1939).

Only a very rough orientation of the abundance of the elements in interstellar space is possible. It is known that hydrogen is by far the most abundant element therein. Swings and Rosenfeld (1937)

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found that numerous diatomic molecules made up of cosmically abundant atoms, such as H_2 , OH , CH , NH , O_2 , CO , CN , etc., should not be much less abundant than Na or Ca^+ atoms in interstellar space. They estimated that there are between 1 and 10^{-3} atoms of hydrogen, carbon, nitrogen, and oxygen, and less than 10^{-14} molecules of carbon dioxide per cubic centimeter in interstellar space. The abundance of a number of cosmic particles is presented in Table 9.4. The values for the concentration of the cyanogen and hydrocarbon molecules are the averages found by Dunham (1941) between seven early B-type stars and the Solar System. The values showing the

TABLE 9.4
ABUNDANCE OF COSMIC PARTICLES
IN INTERSTELLAR GAS

PARTICLE	DUNHAM	STRUVE
	No. of Particles per Cubic Meter of Interstellar Gas	
Electron	11,000,000	
H.	$\lesssim 1,000,000$	2,000,000
O		1,000
Na	107	0.8
K.	10	
Ca	$\frac{1}{2}$ 8	0.12
Ti	< 0.05	
CH.	0.4-3.4	
CN.	$< 0.3-1.8$	

abundance of some atoms are those given by Dunham (1939*b*) for the interstellar space between the Earth and the star χ^2 Orionis and by Struve (1941). Dunham's and Struve's values are, in addition, compared with the abundance values for the Sun's atmosphere and for the gaseous nebula NGC 7027, which has been analyzed by Bowen and Wyse (1939; see chap. 2). All these abundance values are presented in Table 9.5, which is quoted from Struve (1941).

A comparison of Dunham's and Struve's values shows that there are real differences in abundance between the different parts of interstellar space. According to Spitzer (1948), the density of neutral sodium in the opaque interstellar clouds is about $5 \cdot 10^{-8}$ atoms per cubic centimeter if averaged over the space in and between the clouds; but inside the clouds the density probably is about ten times as high, and in the less opaque clouds the density of the neutral sodi-

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um is approximately $2 \cdot 10^{-9}$ atoms per cubic centimeter. In like manner Strömgren (1948) found that the maximum number of hydrogen particles per cubic centimeter in interstellar gas between cosmic clouds is 0.1, whereas in the interstellar clouds the corresponding

TABLE 9.5
COMPARISON OF COSMIC ABUNDANCE OF SOME ELEMENTS

PARTICLE	INTER- STELLAR GAS (STRUVE)	INTER- STELLAR GAS (DUNHAM)	SUN	NEBULA NGC 7027
	Logarithm of Number of Particles per Cubic Centimeter			
Electron	0 2	1		
H.	0.2	1	0	0
O.	-3		-1 5	-2
Na.	-6	-4	-3 3	-4
K		-5	-3 7	-5
Ca	-7	-5	-3 8	-4
Ti.		-7	-5 3	-4

average number is 10. Sodium is also rather strongly concentrated in the clouds, in which its most probable average density is about $4 \cdot 10^{-5}$. The upper limit of its density between the clouds is $1.5 \cdot 10^{-7}$.

The values presented in Table 9.5 show that the composition of the interstellar gas is roughly similar to the composition of the Sun and of the gaseous nebula. It is very probable that the Sun and the other main sequence stars also have the same relative composition as the interstellar matter with reference to the other elements.

OUTLINE OF THE GEOCHEMICAL EVOLUTION OF THE EARTH

INTRODUCTORY REMARKS

ALL geochemical hypotheses dealing with the chemical composition of the Earth share the property of being merely guesses and approximations. Although a concentric structure of the Earth is in accord with known geophysical data, it is impossible to decide which among the suggested Earth models meets the few known facts in the most satisfactory way. Traditional geochemical speculation deals with the formation of the Earth very much according to the experiences gained from the processes taking place in ore-smelting furnaces. The formation of a metal core, a sulfide and a silicate phase, and a gaseous envelope is postulated. On the other hand, the new hypothesis presented by Kuhn and Rittmann (1941) deals with an interior of the Earth which, they claim, consists of compressed solar material rich in hydrogen and helium and is surrounded by a layer very rich in iron and the heavy atoms. A silicate crust encircles the whole.

The two models will be considered in the following discussion. It must be noticed that the geochemical evolution of the Earth did not stop with the formation of a solid crust of the Earth, the hydrosphere, and the atmosphere. Actually, the evolution has continued throughout the geological history of the Earth, and new stages were added, e.g., the evolution of the biosphere. The Earth is changeable chemically, and its geochemical evolution still continues today.

PREGEOLOGICAL EVOLUTION OF THE EARTH

The origin of the Solar System and the ultimate formation of the material which today forms the planets do not lie within the domain of geology. These stages and the primordial evolution of the Earth belong to the field of astronomy and astrophysics, and they are usually referred to the astronomical period in the Earth's evolu-

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tion, which preceded geological time. The zero period of geological time may be chosen as the time when a stable crust of the Earth had formed and the geological processes first started on the crust.

No rational explanation of the origin of the Solar System has, so far, been presented. The physical properties and chemical composition of the smaller bodies in the Solar System suggest that they were removed from a very hot source and that they cooled rapidly. The postulate of the speculation dealing with the geochemical evolution of the Earth is that the primitive Earth was a gaseous body, homogeneous throughout, and that it consisted of solar matter which presumably was rich in hydrogen, helium, and other light elements. The present knowledge on the chemical composition of matter in the Sun makes this assumption plausible, and Wildt (1947) concludes that the composition of the original planetary matrix must have agreed closely with the composition of the Sun's interior in order to provide sufficient mass for the planet.

The Earth's present atmosphere is very poor in the atmophile elements if compared with the Sun's atmosphere. This circumstance strongly suggests, as has been pointed out by Russell (1935), that the Earth was very hot for a short time during its independent existence. The chemical composition of the atmospheres of the other planets affords additional proof of the validity of this view.

Thermal dissipation in the beginning of the evolution of the Earth preferentially caused the loss of the lighter atoms. This process has caused a rapid change in the composition of the original material. The earliest astronomical history of the cooling Earth is terminated by the onset of condensation. According to ter Haar (1948), the Earth, like the other planets, was originally surrounded by an extensive gaseous layer. Three processes took place during the condensation, viz., the formation of condensation nuclei, the growth of the nuclei, and gravitational capture which proceeded at a more rapid rate than did the first two processes. The formation and growth of the nuclei is analogous to the formation of droplets in a supersaturated vapor. Precipitation of supersaturated bodies continued until the bodies grew so large that gravitational effects became important. This caused capture of gas molecules until none was left, but the capture was important only in the case of the giant planets, which have large masses.

The start of the condensation marks the beginning of the first stage of the geochemical differentiation of the Earth (Goldschmidt,

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1926, 1929, 1933*b*), whereby the original gaseous mass differentiates into a gaseous phase and a liquid phase, which is thereafter decomposed into several melts only partially miscible with one another. The liquid phase forms a core which consists of compounds with high boiling point. The gaseous phase is the Earth's first atmosphere or the protoatmosphere. It contains chemically inert and readily volatile elements and other elements in the form of volatile compounds of high chemical stability.

The scientists who believe in the existence of an iron-nickel core of the Earth are unanimous in their opinion that the conditions were such that iron must have condensed into a liquid and that the iron drops fell toward the center of the Earth (Mercier, 1938; Daly, 1943; Eucken, 1944; Baumgartner, 1945; Eskola, 1946). The liquefaction starts in the outer regions of the gaseous globe but probably does not extend to the center of the mass. Even though the liquefaction has been of short duration, it is an important step in the evolution of the Earth.

The chemical composition of the separating liquid phases has been discussed in detail by Tammann (1923, 1924*a*) and Goldschmidt (1926, 1929, 1933*b*, 1945). Their discussion and conclusions are based on the study of phenomena taking place in ore-smelting furnaces. The speculation starts with the postulate that the primitive Earth is an incompletely oxidized mixture of metals and silicon. They further assume that the distribution of the elements is ruled by equilibrium reactions between the adjacent liquid phases believed to be formed. This theory, as a matter of fact, explains the observed distribution of the elements in the meteorite phases.

As pointed out in chapter 4, sulfur- and arsenic-bearing copper ores form pig iron, copper matte, and slag during the smelting—i.e., a metal, a sulfide, and a silicate phase. The processes of the formation of the geospheres are believed to be comparable, to a certain extent, to the separation of the three phases in an ore-smelting furnace. The distribution of the elements among the three phases is governed by their chemical and physicochemical properties. The distribution of the elements among the various phases is essentially controlled by their affinity for oxygen and sulfur and by their latent heat of vaporization (Goldschmidt, 1945). In these respects the elements are compared with iron, which is the most common heavy metal in terrestrial matter. The elements which go into the metal phase are those which have a lower affinity for oxygen and sulfur than iron does and which

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are, as such or in form of compounds, readily soluble in molten iron. These elements are siderophile.

Goldschmidt (1926, 1929, 1933*b*) postulated the existence of a chalcosphere which would incorporate the elements having a higher affinity for sulfur than for oxygen. However, observational evidence for the existence of this layer is insufficient, and a comparison with the meteorites reveals the relative scarcity of a sulfide phase within them. Even though the lack of sulfide meteorites has been explained as the result of complete oxidation of such bodies during their flight through the Earth's atmosphere, little proof is available of the existence of an independent sulfide layer in the Earth. However, it is reasonable to suppose that a sulfide phase was actually formed and that it was dissolved in both the iron and the silicate phases. During the cooling of the silicate phase, the sulfide phase separated as droplets or larger masses. The sulfide phase incorporated the bulk of the chalcophile elements, which, according to their high affinity for sulfur, form sulfides which are readily soluble in the iron monosulfide melt.

The silicate phase, separated from the original liquid phase on cooling, floats on top of the molten iron-nickel core. It consists chiefly of silicates of the light metals, i.e., of elements which have a high affinity for oxygen—in other words, which have a higher free energy of oxidation than iron does for the lowest oxides involved. The silicate phase is not pure because drops of the siderophile elements still separated after the formation of the iron core and fell toward the center. In like manner the silicate is contaminated by segregated sulfides.

A considerable amount of iron, as ferrous silicate, is present in the silicate phase. This shows that, even though the formation of the Earth took place essentially in a reducing atmosphere and oxygen did not suffice to oxidize all the elements present, the amount of available oxygen was sufficient to combine with a considerable proportion of iron, along with silicon and the light metals.

According to Daly (1943), it is possible that much hydrogen and other volatile gases was trapped in the interior of the condensing gaseous body. Therefore, the upper layer of the iron core may be relatively rich in dissolved hydrogen and the other gases.

The general geochemical character of a great number of elements is pronounced enough to cause their decided concentration in one of the separate phases. Thus, e.g., silicon is very strongly lithophile.

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However, many elements are distributed among the phases less quantitatively.

The second stage of the geochemical differentiation of the Earth includes the further evolution of the silicate phase and finally leads to the formation of a solid crust of the Earth, which terminates the pregeological evolution. This differentiation is still going on today. The gradual cooling of the liquid silicate shell released the processes of fractional crystallization, which caused the arrangement of the silicate phase according to the density of the crystallizing phases. The size of the atoms and ions is the ruling factor in the fractional crystallization, and it causes the sifting and sorting of the particles. The crystallization of the silicate melt is usually divided into the following stages (see chap. 5): the separation of early crystallates; the main stage of crystallization; and the crystallization from residual melts and solutions. These processes lead to the formation of rock-making minerals and of igneous rocks.

The elements which are connected with the early differentiates of silicate magmas, e.g., Cr, Ni, Co, Mg, Ti, Fe, V, and the platinum metals become preferentially enriched in the deeper parts of the silicate mantle. However, too big and too small ions are enriched, according to the laws of crystal chemistry, into the residual melts and liquors. The low-density residual magmas of granitic and nepheline syenitic composition and the aqueous residual solutions tend to rise upward. Moreover, pneumatolytic mineralization, caused by gases and vapors, and hydrothermal and metasomatic mineralization from aqueous residual solutions may concentrate heavy atoms into the uppermost parts of the silicate phase, e.g., uranium and thorium, which actually should become concentrated in the lower levels of the lithosphere. These processes consequently counteract the differentiation phenomena which endeavor to concentrate heavy atoms and crystals and melts of high density toward the Earth's interior and which tend to make the upper lithosphere impoverished in heavy metals.

It is probable that the first stage in the geochemical differentiation of the Earth was of short duration as compared with the second phase, which caused the formation of the solid crust (Eskola, 1946). All through the second stage the differentiation by crystallization continued in the forming crust, and the process still goes on today. It is probable that this process has been the main factor in the arrangement of the lithosphere. The rise of the melts and liquors of low den-

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sity and the sinking of the high-density melts and crystallates has caused the grading of the original lithosphere into different layers according to the density of the various phases. This process also gives a clue to the explanation of the present-day distribution of the elements in the upper lithosphere.

Adams (1924) was the first to conclude that the solidification of the silicate mantle proceeded from the bottom up. Wasiutyński (1946) thinks that, although the solidification started at the bottom, the surface of the uppermost granitic layer solidified first, whereas the lower strata of the layer were liquid still in the Archean, and that the final crystallization took place during the Caledonian revolution.

Nearly all geologists, geophysicists, and geochemists have adopted the theory of the existence of an iron-nickel core. However, Kuhn and Rittmann (1941; Kuhn, 1942, 1946; Rittmann, 1947) deny the existence of the metal core on the grounds that, for the Earth as a whole, a gravitational separation is impossible because the viscosity of the material was too high. Moreover, the time since the Earth's formation has been too short to permit the attaining of mechanical and chemical equilibrium in the Earth, although this is possible in smaller astronomical bodies. Therefore, they resort to a homogeneous model of the Earth (see chap. 3). The present state of the Earth is a result of an asymptotic process, which means that the iron core could have formed during the last stages of the evolution, when the temperature, pressure, and viscosity of the Earth's interior were essentially similar to those prevailing therein today. However, the present physical properties of the Earth's interior do not make the formation of an iron core possible. The conditions necessary for the formation of an iron core existed only during a very short time and only in the outer parts of the condensing Earth. Therefore, a passive enrichment of iron which would lead to the formation of an iron core cannot be possible.

According to the theory set forth by Kuhn and Rittmann, much hydrogen and helium originally found in the terrestrial material escaped into space during the earliest stages of the Earth's independent existence. The outer regions of the gaseous mass cooled, whereas the inner parts attained a high temperature. Therefore, convection currents started to carry gas masses heavily laden with hydrogen toward the surface. This caused degassing, the most important differentiation process in the Earth, whereby the gas masses were deprived of their lightest constituents. The peripheral gases sank back toward

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the deeper levels, where homogenization took place. The degassing was limited to the uppermost gas masses. When the temperature of the outermost layers decreased, a number of oxides and metallic iron, which was not oxidized because much hydrogen was present, condensed and sank downward as droplets, causing the formation of a layer of only slightly volatile substances. The result of these processes was the formation of a liquid shell resting on highly compressed, nearly unchanged solar matter rich in hydrogen. The degassing continued as gas bubbles rose through the liquid. This caused an intensive effervescence. During further cooling, the outermost layers started to crystallize, and a differentiation by crystallization, even though on a very limited scale, took place. The present-day volcanic activity is a sequel to the intensive effervescence of the pregeological times. The time of existence of the Earth as an independent body is too short to allow a notable escape of hydrogen by diffusion from the inner parts toward the surface.

Kuhn (1942, 1946), however, agrees that the gravitational differentiation of the silicate mantle claimed by Tammann and Goldschmidt has been and still is very important, whereas the high temperatures and pressures in the innermost parts of the Earth make any separation of phases practically impossible, because increase in temperature and pressure promotes the mutual solubility of the phases. Neither at present nor during the earlier stages of the Earth's evolution have the circumstances favored the contemporaneous formation and separation of droplets of liquid iron and sedimentation of iron to form a metallic core. Although the convection currents promote differentiation processes taking place on the surface, they reduce and prevent those which would take place in the deeper regions where no currents normally should occur.

According to Kuhn (1946), the separation of iron from the highly compressed solar matter is possible only in the surface layer of the Earth. The reason is that hydrogen readily dissolves in molten iron at elevated temperatures. Under certain circumstances all available hydrogen will dissolve, and a supercritical state is reached. Thus, in a mixture consisting of 90 per cent hydrogen and 10 per cent iron at a temperature of $5,000^{\circ}$ K. and a pressure of $2 \cdot 10^6$ atm, hydrogen is completely absorbed by iron. Therefore, it follows that the formation of a liquid-iron core in the primitive planet may take place only if the mass of the planet is small enough to let most of the hydrogen escape.

The hypothesis of Kuhn and Rittmann is based on the assumption

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that the conditions necessary for the formation of an iron core existed only when the interior of the Earth had already obtained its present physical properties. This has given rise to the argument presented by Eucken (1946) that the core might form in a relatively early stage of the evolution and that a liquid core might separate by condensation directly from a gaseous phase. As emphasized by Eucken, Kuhn and Rittmann have shown that the manner of formation of the iron core so far suggested is not comparable to the processes in an ore-smelting furnace.

A geochemically interesting argument against the hypothesis of Kuhn and Rittmann was presented by Eskola (1946), who pointed out that certain elements, in particular silicon, aluminum, and the alkali metals, have migrated toward the surface and now are rather strongly enriched in the upper lithosphere. The matter which has migrated toward the surface constitutes a large part of the total mass of the Earth, and therefore one must reckon with a differentiation down to the Earth's interior. Consequently, hydrogen, a light and mobile element, must, *a fortiori*, have followed along with the Sial substance.

FORMATION AND EVOLUTION OF THE LITHOSPHERE

The early stages of the formation of the lithosphere were dealt with in the preceding paragraph. Two groups of processes affecting the composition and evolution of the lithosphere may be separated—the processes taking place within the lithosphere, particularly in its uppermost parts, and those modifying the composition of the relatively thin surface layer. The first of these groups has been active since the second stage in the geochemical differentiation of the Earth and is still active. The phenomena of the second group started with the formation of the first stable crust surrounding the Earth. Also in the case of the lithosphere one must reckon with the two hypotheses concerning the composition of the Earth's interior. Consequently, the following discussion will deal first with the traditional geological and geochemical discussion on the origin and formation of the lithosphere, followed by the presentation of the recent hypothesis of Rittmann (1947). The highly speculative suggestions of Dauvillier (1947) are supported by few known facts and consequently will not be included in this paragraph.

The formation of the solid crust terminated the pregeological evolution of the Earth. The formation of the crust included numerous

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phases of remelting until a stable crust was formed. Thereafter, light granitic magmas began their rise upward, and the isostatic adjustment of the Earth's crust was finally established. It is probable that the crust originally was very thin, perhaps only a few hundred meters in thickness (Eskola, 1932*a*). The thickness increased by the action of intruding and solidifying granitic magma masses, and it might be probable that in Archean times there occurred a regional upwelling of granitic magmas (Eskola, 1936). During the earliest stages of geological evolution, volcanic activity probably was very pronounced, and also plutonic activity took place on a larger scale than it ever did later.

When the temperature of the crust was still high, above the critical temperature of water vapor, chemical reactions took place between the crust and the atmosphere. Before the condensation of water vapor the reactions had the character of pneumatolytic reactions, but, with the condensation and the drop in temperature, they declined in intensity and assumed the character of hydrothermal activity. Finally, the hydrothermal reactions graded over to weathering. It is thus evident that intense chemical decomposition of the Earth's first crust has taken place.

The start of weathering marks the onset of the third stage in the geochemical differentiation of the Earth (Goldschmidt, 1926, 1929, 1933*b*). This stage consists of the exogenic cycle and is represented principally by the formation of sediments and sedimentary rocks. Secondary alteration processes and metamorphic phenomena are also included in this group, and they all share the property of taking place in aqueous solution. The exogenic cycle grows in activity with the formation of the hydrosphere and the evolution of an atmosphere containing free oxygen.

The crystallization from the aqueous solutions, whether of juvenile or of meteoric origin, takes place at temperatures which are considerably lower than the temperatures at which the crystallization of magmas takes place. Consequently, the thermal order of the three stages of geochemical differentiation corresponds to their chronological order. Temperature, pressure, hydrogen-ion concentration, and redox potential govern the crystallization from aqueous solutions. Crystal structure, ionic dimensions, and colloid chemical phenomena determine the distribution of the elements in the various geochemical groups of sediments (see chap. 5).

The reactions taking place between the rocks on the Earth's sur-

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face and water and oxygen, which are the most important active constituents of the hydrosphere and the atmosphere, may be repeated and will finally lead to a closed cycle, contrary to the first stage of geochemical differentiation, which took place only once and in a given direction. In this respect they also differ from the early part of the second stage of differentiation.

The processes which have caused inhomogeneity of the Earth and still cause migration of elements and their compounds may be called the metabolism of the Earth (Goldschmidt, 1922*b*). Mechanical and chemical weathering, transportation, and sedimentation cause a separation of most of the chemical constituents of rocks. Goldschmidt compared these processes with a gigantic semiquantitative chemical rock analysis. Even though the result is not very bad, it is not very good, either, because the methods of analysis are not refined.

Material from the outer crust enters the endogenic cycle in mountain-building processes. Metamorphic and metasomatic processes thereby start to modify the composition of the added material. Metamorphism is active in the present-day evolution of the upper lithosphere, just as it was before. As pointed out by Goldschmidt (1922*b*), the general tendency in metasomatic processes is toward equalization of the composition of the lithosphere. However, this tendency is not very pronounced because many processes, e.g., radioactive decay, lead to a new differentiation. The products formed by metamorphic and metasomatic changes may re-enter the exogenic cycle. Therefore, it is evident that there is a considerable amount of matter in constant circulation, which causes an increasing chemical differentiation. Metasomatic processes are unable to equalize the composition of participating material. At present, differentiation predominates over the equalization in the Earth as a whole. Progressive differentiation will take place until the cooling of the Earth's crust terminates it, at least temporarily.

Along with the metamorphic and metasomatic processes, plutonic and volcanic processes change the composition of the upper lithosphere. In the arrangement of the outermost silicate shell of the Earth, crystallization and differentiation by crystallization were and still are the most important processes. The light granitic magma, which has a low temperature of crystallization, still wanders upward through the crust (Eskola, 1939*a*).

The bivalent oxygen is the only important anion in the lithosphere (Goldschmidt, 1928). The lithosphere is actually an oxy-

sphere: the oxygen content in the upper lithosphere is 91.83 per cent by volume (see Table 2.2). According to Ramberg (1944, 1946*b*), oxygen and other elements with low fictive density move upward in the crust, whereas elements with high fictive density migrate downward. The migration is caused by diffusion. Consequently, highly oxidized surface rocks, when brought down into the deeper parts of the upper lithosphere, lose a part of their oxygen by squeezing. The oxygen returns to the surface, partly in minerals, partly as water and carbon dioxide (Barth, 1948). Atomic oxygen might form at high temperatures and pressures. The rocks are oxidized at the surface during weathering, and the weathering products are deprived of a part of the oxygen in the depth. Because iron is the main constituent to become oxidized (to ferric iron) and reduced (to ferrous iron) in these processes, it acts as a respiratory pigment in the upper lithosphere, as pointed out by Landergren (1948).

Not only oxygen is squeezed out from the rocks in the deeper layers of the Earth's crust, but water is expelled from hydrous minerals, partly as water molecules, partly as hydrogen and oxygen ions (Ramberg, 1948). Moreover, carbon dioxide may be removed from carbonate minerals and limestones.

Ramberg (1945*c*) suggests that there exist chemical potentials which are responsible for the gravitative arrangement of the various minerals into homogeneous spheres and which act in the same direction as do the gravitational force. If rocks or magmas of high density rest on rocks or magmas of low density, chemical potential differences exist which tend to cause the masses to change places. Ramberg (1948) also believes that diffusion is the only process able to equalize chemical instability in the upper lithosphere.

The processes referred to above which take place in the interior of the lithosphere have tended, during the geological history of the Earth, to equalize any differences in the distribution of the elements. The primary distribution of the elements in the various layers of the upper lithosphere might originally have been uniform in all parts of the globe, provided that no primordial differentiation had taken place to cause differences. At present, there are numerous examples of the inhomogeneity of the upper lithosphere, many of which are referred to in Part II of this book. Among the most notable is the high abundance of uranium and radium in some parts of the pre-Cambrian Canadian Shield and the scarcity of these metals in the pre-Cambrian areas of Fennoscandia. Similarly, there are regional

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differences in the content of strontium and barium in igneous rocks (Holmes and Harwood, 1932). The differences are very marked in granites of different geological ages and of different geological formations. The general rule seems to be that granites of very ancient geological age are markedly deficient in many trace elements, compared with chronologically younger granites. To explain this peculiar behavior of the granites, it has been suggested that a secular migration of the elements on a global scale takes place in the Earth's crust and leads to a geochemical differentiation of the upper lithosphere (Ran-kama, 1946). A group of elements, called the granitophile elements, which are typical of the light granitic magmas, tend to become concentrated in the outermost parts of the lithosphere. This group includes, among others, lithium, rubidium, cesium, beryllium, lanthanum and the lanthanides, columbium, and tantalum. The siderophile and chalcophile elements, along with some other elements which are called granitophobe, are pushed down toward the basaltic substratum. The explanation of the global differentiation is the continuous self-repeating granitization which is believed to take place in connection with the mountain-building processes. The intergranular palingenetic granitic magma tends to rise toward the surface, in some cases rejuvenated and augmented by residual primary granitic magmas. The granitization, along with the slow chemical processes which endeavor to attain complete thermodynamic equilibrium during the evolution of the crust—dispersion, migration, and consolidation (Ramberg, 1945*a*)—is thought to be reproduced throughout the orogenic history of the Earth. The continuous formation of granites, whether truly magmatic or palingenetic, will greatly add to the silicic character of the outermost layers of the lithosphere. It must be noticed that granites and granodiorites now constitute 95 per cent of all known areas of intrusive rocks.

The discussion presented above is based on traditional geological and geochemical speculation. The formation and evolution of the outermost geochemical spheres of the Earth on the basis of the hypothesis of a hydrogen-core Earth were discussed by Rittmann (1947) on the basic assumption that the subcrustal magma cannot produce a granitic residual melt during differentiation, but only a trachytic or phonolitic melt. Therefore, the first Sial crust must have been of a nonmagmatic origin. According to Rittmann, the fluid silicate layer on top of the solar matter in the interior of the Earth consisted chiefly of silicates of magnesium and of small amounts of silicates of

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iron, calcium, and the alkali metals. Water vapor and hydrogen were also present in the melt. This composition corresponds to an olivine basalt magma. Convection currents took place and removed water vapor, hydrogen, and other readily volatile substances, e.g., chlorides of the alkali metals. These compounds were transported to the surrounding gaseous phase, called the pneumatosphere, which consisted chiefly of hypercritical water vapor and notable quantities of nitrogen, hydrogen, carbon dioxide, and hydrochloric acid. Moreover, there were readily volatile chlorides, fluorides, and other compounds. The pneumatosphere had the properties of a pegmatitic-pneumatolytic solution, and consequently it was able to incorporate considerable quantities of so-called pneumatophile elements, i.e., those which become enriched in pegmatitic, pneumatolytic, and hydrothermal solutions and are carried by gases and vapors. This group includes many chalcophile and lithophile elements. Rittmann believes that all these elements were more or less completely removed to the pneumatosphere simultaneously with the formation of the fluid magma layer.

The crystallization of the magma layer started from the surface and finally produced a solid crust of olivine basaltic composition. When the temperature of the pneumatosphere decreased below about 800° C., quartz, feldspars, and micas separated and settled on top of the solid silicate layer, as a pegmatitic crust. This was covered mainly with quartz when the temperature sank to approximately 400° C. The silicic layer was penetrated by frequent eruptions of the basic subcrustal magma. The pneumatolytic deposits, in particular, contained minerals formed in the pneumatosphere by supersaturation, such as cassiterite, molybdenite, and wolframite. The sulfide minerals of lead, zinc, silver, mercury, and other metals remained in the hydrothermal solution until condensation of the water vapor took place.

This condensation also caused strong mechanical and chemical weathering in the beginning of the process, when the temperature was around 100° C. The silicate minerals were decomposed and dissolved. Quartz, argillaceous substances, sericite, and chlorite were deposited in the basins of the primordial oceans. Hydrothermal minerals, such as calcite, magnesite, and siderite, were also formed, making the Protosial, which had a gabbroic or dioritic composition.

A part of sodium and small amounts of potassium, magnesium, and calcium were removed in solution to the hydrosphere, but the bulk

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of the pneumatophile elements was present in the Protosial. The minerals which dissolved or decomposed only with difficulty became concentrated locally as placers in the sediments, and this process caused the uneven distribution of tin, tungsten, lead, zinc, copper, and other elements in the Protosial and later in the ore deposits in the uppermost lithosphere. The small remainder of the pneumatosphere formed the atmosphere, which developed gradually into the present atmosphere, owing to the passive enrichment of oxygen and removal of hydrogen by dissipation. Radioactive decay produced the heat required for the partial melting and anatexis of the Protosial, and only then was the first granitic magma produced. This process, again, caused the migration of the bulk of the pneumatophile elements toward the surface. The upwelling material and the metamorphosed sediments formed the Sial crust in a process of metamorphic differentiation, and, finally, the lithosphere obtained its present composition and structure.

FORMATION AND EVOLUTION OF THE ATMOSPHERE

The formation and evolution of the atmosphere is of high geochemical interest. As a matter of fact, the processes connected therewith are less hypothetical than those envisaged for the evolution of the lithosphere. The processes and phenomena connected with the formation of an atmosphere for the hydrogen-core Earth were presented in the previous paragraph, and therefore it remains to discuss the evolution of the atmosphere on the basis of other, traditional, viewpoints.

The first stage of the geochemical differentiation included the formation of a gaseous phase, the protoatmosphere, which surrounded the liquid phase. The protoatmosphere contained chemically inert and readily volatile elements and compounds of other elements having these properties. Prior to this stage the Earth must already have lost a very large amount of the lighter atoms by dissipation into space. Russell (1935) concludes that the cooling of the Earth has been so rapid that surface temperatures of the order of 5,000° K. could not have prevailed for more than a few years. Consequently, the loss of the light and inert elements must have taken place during the first years, if not days, of the Earth's independent existence. It seems to be probable that the Earth actually lost most, if not all, of the original atmospheric constituents during an early stage in its evolution, immediately or almost immediately after its separation as an independent body (Russell and Menzel, 1933). Therefore, the present

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atmosphere and the present hydrosphere probably are of secondary origin (Goldschmidt, 1926; Russell, 1935; Lord Rayleigh, 1939).

Kuhn and Rittmann (1941) calculated that, as long as the surface temperature of the Earth exceeded $6,000^{\circ}\text{C.}$, all elements with atomic weight up to 30 would escape from the gravitational field. At a temperature of $3,000^{\circ}\text{C.}$ the limiting atomic weight would be 14; at $2,000^{\circ}\text{C.}$, 10; at $1,500^{\circ}\text{C.}$, 7; and at $1,000^{\circ}\text{C.}$, 5. Moreover, free electrons escape readily from the upper layers of the gaseous mantle, and therefore these layers will receive a positive charge, which increases the rate of escape of positively charged ions. Therefore, for positive ions the effective limiting atomic weight is about half the real atomic weight. Such elements as sodium, potassium, and calcium, which are readily ionized, will thus be removed.

The elements present in the protoatmosphere included the typically atmophile elements hydrogen, nitrogen, and the inert gases; carbon as carbon dioxide; and such elements as mercury, sulfur, selenium, tellurium, and arsenic, which either are readily volatile or, together with hydrogen, form gaseous molecules and radicals. Also, the halogens chlorine, bromine, and iodine may have been present as hydrogen compounds (Goldschmidt, 1926, 1937*b*). The presence of sulfur and chlorine in the protoatmosphere had already been suggested by T. Sterry Hunt in 1897. Eucken (1944) points out that hydrides, including the silicon hydride, must actually have been very abundant in the gaseous mantle because of the high abundance of hydrogen. They were later decomposed or oxidized, and hydrogen escaped into the interplanetary space. In like manner the alkali metals, being readily volatile, were originally present in the gaseous mantle.

When the liquid silicate shell began to solidify, great quantities of gases escaped from the crystallizing melt into the rarefied gaseous sphere. The new atmosphere escaped at a slower pace, and the rate of escape decreased with the continuing cooling of the Earth's surface. The atmosphere would consist of carbon monoxide and dioxide, nitrogen, water vapor, the inert gases, and some leftovers from the protoatmosphere. In addition, the preaquatic atmosphere contained compounds having critical temperatures greater than the critical temperature of water vapor, e.g., halogen and sulfur compounds, such as SO_2 , SO_3 , and H_2S , and a number of compounds of boron, arsenic, and mercury, and ammonium salts. These compounds were removed from the atmosphere before the condensation of water va-

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por. It is unlikely that at this stage the atmosphere contained large amounts of free oxygen. It must be noticed that free oxygen is not a characteristic constituent of volcanic emanations. In like manner igneous rocks contain ferrous iron as a proof of their deficiency in oxygen.

The next stage in the evolution of the atmosphere consisted of the condensation of water vapor when the temperature decreased below the critical temperature of water vapor. This process will be discussed in the next paragraph.

Geochemically, the most important process in the evolution of the atmosphere is the formation of free oxygen. At present, the presence of large quantities of free oxygen in the atmosphere of a planet is restricted to the Earth. Therefore, it is probable that the formation of an atmosphere containing free oxygen is not a normal feature of planetary evolution.

Three different theories have been presented on the origin of atmospheric oxygen. During the earliest stages in the geological history of the Earth there probably was no free oxygen in the atmosphere. According to Tammann (1924*b*), water vapor in the atmosphere was thermally decomposed into hydrogen and oxygen. Hydrogen escaped into space, and oxygen was first consumed in the oxidation of ferrous silicates when the solidification of the Earth's crust still was incomplete. Only when a solid crust was formed did oxygen accumulate in the atmosphere. Tammann believes that free oxygen was probably formed between the start and the end of the solidification of the crust. Kuhn and Rittmann (1941) also favor this manner of formation of the atmospheric oxygen. However, according to Niini (1932), the decrease of temperature after the formation of the second atmosphere containing water vapor has been so rapid that the outermost layers of the atmosphere have cooled off enough to make the thermal dissociation of water vapor improbable.

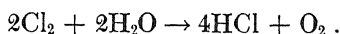
Another theory of the origin of the atmospheric oxygen was presented by Goldschmidt (1933*a*, 1934), who based his discussion on the production of vast amounts of oxygen in the photosynthetic processes by green plants at the present time. He concluded that most or all free oxygen has been gradually produced from carbon dioxide by photosynthesis. The bulk of carbon dioxide which has participated in the cycle of carbon is the gradual product of volcanic activity. However, when the first chlorophyll-bearing plants evolved, there must already have existed at least a small initial supply of free at-

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mospheric oxygen to make the respiration of the plants possible. It is not necessary for this supply to have been great because even today a small proportion of the present content of atmospheric oxygen would suffice to meet the needs of plant life.

According to the third theory, the small initial supply of oxygen is a product of photochemical dissociation of water vapor rather than of thermal dissociation (Eskola, 1939; Poole, 1941). Thereafter, the bulk of the present-day atmospheric oxygen was produced by photosynthesis, as is generally believed today.

Additional oxygen may have been produced in some reactions taking place between volcanic gases, as pointed out by Nichols (1941):



However, a part of the oxygen thus liberated is consumed in the oxidation of other constituents of volcanic emanations, and the quantitative importance of this source remains unknown. Provided that temperature was sufficiently high during the earlier stages of the Earth's evolution, gravitative differentiation in the lithosphere might have contributed to the supply of free oxygen by squeezing oxygen out from mineral structures (Ramberg, 1948). However, this oxygen may have been consumed in oxidation and never have reached the surface.

As pointed out above, carbon dioxide has probably been gradually added to the atmosphere by volcanic emanations. Biological arguments favor this view. Conway (1943) has calculated that the total amount of carbon dioxide bound within carbonates and bioliths and in the biosphere would give a partial pressure of about 480 mm Hg if it were all present in the atmosphere. This high carbon dioxide concentration is fatal to life. However, other sources of carbon dioxide have also been suggested. Noddack (1937) thinks that the carbonates might have been formed by the oxidation of native carbon after the formation of a solid crust. The relatively high content of carbon in stony meteorites, compared with the terrestrial igneous rocks, would seem to lend support to this view. Noddack also suggests that atmospheric carbon dioxide was produced in reactions between silica and carbonates during the solidification of the crust. Conway (1943), in part following Poole (1941), suggested that methane of volcanic origin or primarily found in the atmosphere was oxidized into carbon dioxide or removed directly by biochemical agencies.

Högbom (1894) was the first to reason that considerable change in

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the carbon dioxide content of the atmosphere is possible. At the present time much carbon dioxide is added to the atmosphere as a result of combustion of various carbonaceous fuels and of fermentation in the anthroposphere (see chap. 19). The content of carbon dioxide in the atmosphere is now on the increase and will continue to be so until the difference in the partial pressure of carbon dioxide between the atmosphere and the sea—the regulating mechanism—has grown large enough to produce equilibrium or a steady state at which carbon dioxide is absorbed by sea water at the same rate at which it is produced. At present, the amount of carbon dioxide produced by combustion exceeds the amount stored in the caustobioliths (see Table 19.4).

All carbon dioxide is finally bound as carbonate during the weathering of igneous rocks, and chances are small that it will ever become completely released in silicification. The progressive cooling of the Earth makes the formation only of compounds of low energy content possible, as Högbom (1894) points out, and the fixation of carbon dioxide in carbonates is one of those processes. The other chemical reactions which take place in the zone of weathering are predominantly of similar character.

Like carbon dioxide, nitrogen also might be largely of juvenile origin. The nitrogen in volcanic gases is evidently partly of meteoric origin, but an ample supply of nitrogen is present in igneous rocks (Lord Rayleigh, 1939). This suggests that atmospheric nitrogen is not necessarily a residue from the protoatmosphere. The supply increased during geological time, when nitrogen trapped in rock minerals was released. Ammoniacal nitrogen is probably also present in igneous rocks. It is probable that both molecular nitrogen and ammonia were present in the atmosphere after the formation of the solid crust (Hutchinson, 1944). Nitrogen oxides might have been produced in photochemical reactions and electrical discharges.

The inert gases in the atmosphere may be assumed, with a high degree of probability, to be produced by volcanic emanations and weathering of rocks. The bulk of these gases was lost during the initial stages of the evolution of the Earth. The exceptionally high abundance of argon is caused by the formation of the isotope A^{40} in the radioactive decay of K^{40} during the geological evolution of the Earth (see chap. 45). As pointed out by Russell and Menzel (1933), there is practically no hydrogen in the present atmosphere and much less helium than has been liberated from radioactive igneous rocks

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during geological time. Hydrogen and helium are still being eliminated today from the upper atmosphere by collision with metastable oxygen atoms, which impart to hydrogen and helium atoms speeds which exceed the escape velocity.

According to the discussion presented above, it is certain that the composition of the Earth's atmosphere has changed during geological evolution. Very probably the whole present atmosphere is of secondary origin. Even today the chemical composition of sea water still displays some of the features of the ancient atmosphere before and during the condensation of water vapor, viz., the high abundance of compounds of chlorine, bromine, iodine, boron, and sulfur, which are rare in the upper lithosphere.

Independent proof of the secondary origin of the present terrestrial atmosphere was furnished by Kuiper (1944) from a study of the composition of the atmosphere of Titan, one of Saturn's satellites. The study revealed the presence of gases rich in hydrogen in Titan's atmosphere. This fact indicates that, if Titan's surface ever was hot, its present atmosphere must be secondary. With almost equal force, this conclusion follows for Mars, which, like Titan, has a small mass, and to a lesser extent for Venus and the Earth. All, or nearly all, present constituents in the atmospheres of these planets must have escaped from the crust after the cooling of the planet.

FORMATION AND EVOLUTION OF THE HYDROSPHERE

The formation of the hydrosphere starts with the condensation of water vapor. Because the present atmosphere is now believed to be of secondary origin, it is only reasonable to make the same assumption for the hydrosphere. Therefore, the primeval hydrosphere must be considered to have been much less massive than the present hydrosphere. On the other hand, the opposite assumption, viz., that the amount of water on the Earth has not changed since the condensation, at least not decreased considerably, has been proved to be useful for theoretical considerations dealing with the process of condensation.

Niini (1932) based a theoretical discussion of the condensation of water vapor on the assumption that the quantity of water has remained stable. He showed that, when the condensation took place, a dense layer of clouds and a phase boundary formed between the liquid and the gaseous water. No rains occurred, but the quantity of the condensed water increased slowly. The condensation started

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when the critical temperature of water was reached. However, the substances partly dissolved in the gaseous phase caused the condensation to start above the critical temperature of pure water. At a temperature of 100° C. the atmosphere still contained much water vapor, and the atmospheric pressure was higher than today. Chemical reactions took place in the vapor phase and also between the atmosphere and the Earth's crust. They resembled pneumatolytic and hydrothermal processes.

However, because the amount of water evidently has been unstable and the present hydrosphere is of secondary origin, the amount of water vapor during the condensation must have been small, and therefore the condensation started below the critical temperature of water, and there actually was a first rain.

At present it cannot be stated whether the amount of water is still increasing. Water vapor is given off by the volcanoes, but it is probably largely of meteoric origin. Water is removed by weathering and sedimentation, and it might be possible that the removal balances, or perhaps exceeds, the addition.

Changes have occurred in the chemical composition of the oceans during the geological evolution of the Earth. The hydrosphere after its formation evidently contained material which was dissolved in the preaquatic atmosphere and deposited on the crust of the Earth. The first salts in sea water were probably mainly halogenides. It might be possible that the primeval ocean was more acid than the present one and that the content of salts in sea water was comparatively low. However, during the geological evolution, many substances accumulated in the ocean, partly produced by weathering of rocks. Moreover, it must be assumed that vast amounts of volatile substances released by volcanic activity were finally transported into the sea. Conway (1943) has calculated that only approximately 2 per cent of the oceanic chloride was produced by weathering, provided that the average composition of igneous rocks has not changed during geological evolution.

Landergren (1945) suggested that the original boron content of the hydrosphere was forty to fifty times as high as the present boron content of sea water. This content would represent the original supply of boron compounds produced by volcanic activity before the formation of the hydrosphere. A continual decrease in the boron content took place until equilibrium was attained between supply and deposition; this had already happened during pre-Cambrian times. From

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Cambrian to Recent time the boron content of sea water has remained practically constant.

According to Conway (1943, 1945, 1947), the content of both sodium and potassium in sea water increased in the beginning, and the peak of the potassium concentration was reached between the pre-Cambrian and the Cambrian. Then the removal of potassium in certain minerals caused the gradual decrease of the potassium content until its present level was reached. Conway suggests that potassium was removed in illite and to some extent in glauconite and phillipsite. The removal in glauconite possibly predominated from the Mesozoic era onward. Conway believes that biochemical processes promote the formation of glauconite, which started in the pre-Cambrian ocean when the organisms were first formed. When potassium was removed, a corresponding amount of hydrochloric acid was released, and an equivalent amount of calcium carbonate was dissolved. Therefore, there occurred a progressive increase in the calcium and magnesium content of ocean water until the Cambrian, when the first calcareous shells appeared. Parallel to the increase in the content of calcium and magnesium, the content of sulfate decreased. So far, Conway's views have not been unanimously accepted.

The ocean is effectively buffered against large releases of acid or alkali. The hydrogen-ion concentration, according to Conway (1943), has remained nearly constant.

Sedimentation in the hydrosphere affects the chemical composition of the upper lithosphere. Kuenen (1937) emphasizes the fact that real deep-sea sediments are totally or nearly totally absent on the present-day continents; and therefore he concludes that all material deposited in the depths of the oceans is permanently lost to the cycle. A continuous accumulation takes place in the abyssal regions. Much water is also lost in the pore space of the accumulating sediments, and the loss attained a maximum during the early history of the oceans. Since that time the volume of the oceans has remained practically constant.

Kuenen (1938, 1941) also thinks that the calcium liberated in weathering before the Cambrian was precipitated physically and chemically in the shallow waters of the epicontinental seas. From the Cambrian onward, biological precipitation of calcium carbonate took place, and at present so much calcium is permanently deposited in the *Globigerina* ooze that in about $150 \cdot 10^6$ years a lime famine must set in.

FORMATION AND EVOLUTION OF THE BIOSPHERE

Vernadsky (1933) pointed out that the reactions taking place in the upper lithosphere have remained practically unchanged since the earliest geological history of the Earth. The same minerals were formed in Archean igneous rocks that form in igneous rocks today. Contrary to the stability of the upper lithosphere, the biosphere is changeable.

All organisms contain endothermic compounds. Consequently, they require foreign energy, either cosmic or terrestrial, for their sustenance.

It is not known with certainty when life started on the Earth. Hutchinson (1944) believes that life, atmospheric oxygen, and the ocean all developed concurrently. Baudisch (1943) expressed the belief that life started very soon after the Earth had cooled off to the proper temperature and that it covered the Earth's crust in a geologically short time. The oldest fossil so far known, *Corycium enigmaticum* Sederholm (Rankama, 1948a), is dated, by geological evidence, as far back as no less than $1,400 \cdot 10^6$ years.

It is probable that organic substances were synthesized before the advent of the organisms and that there was a large supply of prebiological organic matter available. The evolution of the organisms depended on the quantity and manner of occurrence of the biophile elements, in particular, on the supply of carbon, nitrogen, and oxygen. Hutchinson (1944), who believes that the ancient atmosphere contained both molecular nitrogen and ammonia, thinks that the utilization of oxidized nitrogen by the organisms is a later process than the utilization of ammonia. The first true organisms presumably were ammonia organisms or lived on the accumulated organic matter left over from their evolution. They converted ammonia into organic compounds (amines). The limited supply of original ammonia was probably augmented by some juvenile ammonia. As soon as oxygen appeared, ammonia was oxidized to nitrate, which accumulated. The evolution of autotrophic nitrifiers would intensify the accumulation of nitrate until organisms evolved which were capable of utilizing nitrate and nitrite, either in place of oxygen in respiration or as a nitrogen source in the protein synthesis. Hutchinson believes that the biological fixation of nitrogen is probably a later phenomenon than the other stages. The development of leguminous plants in the Mesozoic presumably caused an increase in nitrogen fixation, but the

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nodule bacteria grew in importance only with the advent of the scientific methods of agriculture during the Psychozoic era. According to Hutchinson, the present composition of the atmosphere is probably unstable in the presence of solar radiation and meteorological phenomena without nitrate-utilizing and denitrifying organisms.

Eskola (1939) has emphasized the connection between the rhythm in the biological evolution of the Earth and the orogenic movements. During the mountain-building processes the volcanic activity attains a maximum, and during these times also the production of juvenile carbon dioxide may have reached a peak. The orogenic periods in the Earth's evolution are also culmination periods of biological evolution, and therefore one may assume that the abundant supply of carbon dioxide is one of the reasons for the rhythm in the evolution of life and in its evolution as a whole. Carbon dioxide is constantly being stored in limestone, but the deficiency caused by this process is, so far, balanced by juvenile carbon dioxide and, at present, overbalanced by the combustion of carbonaceous fuels. However, life—first and foremost the existence of plants—depends on the production of juvenile carbon dioxide and would soon be brought to a stop if the production should cease.

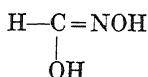
Eskola (1940) has also discussed the mutual relationships between carbon dioxide and oxygen in the atmosphere and the evolution of life. He states that the existence of free oxygen is chemically abnormal because oxygen readily combines with most other elements. Therefore, an oxygen-bearing atmosphere is actually luxury. The condition of its formation is that the carbon dioxide content in the beginning was small, not very much in excess of its present value, because a higher content is lethal to life. Consequently, the plant life must have started before too much carbon dioxide had been released into the atmosphere by volcanic activity. Later, the production of juvenile carbon dioxide was balanced by its removal in biological processes and in weathering, and the content of carbon dioxide in atmospheric air remained constantly low. If life had started too late, it could not have been sustained because of the high carbon dioxide content of the atmosphere and the hydrosphere, and therefore the carbon dioxide content would constantly rise.

The complexity of living matter has increased throughout the geochemical evolution of the biosphere. In this respect the inorganic compounds are unable to compete with the organic compounds. However, it may be assumed that the chemical reactions brought

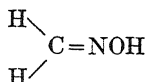
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about by organisms were basically constant through all the geological history since the start of life. Only their intensity has changed with the geological epochs (Baudisch, 1943).

The first organic compounds on the Earth may have been formed by photochemical reactions or by electrical discharges in the atmosphere, provided that suitable inorganic compounds were available. It is known that formaldehyde is present in rain water, and it has been suggested that it forms photochemically from carbon dioxide and water vapor in the atmosphere in or above the ozone layer. The first carbohydrates may have formed from carbon dioxide and water in a photochemically activated synthesis. Baudisch (1939) considers formhydroxamic acid:



and formaldoxime:



the simplest carbon- and nitrogen-bearing compounds formed from inorganic matter in photochemically activated synthesis. Formhydroxamic acid is synthesized from formaldehyde and nitric oxide, and nitric oxide forms in the atmosphere as a result of photochemical oxidation of nitrogen or ammonia or in electrical discharges. Nitrogen might have entered the biosphere in the form of formhydroxamic acid.

Plant life probably could not start until there was some free oxygen in the atmosphere. Photosynthesis cannot have started without the previous existence of living matter. Rabinowitch (1945) believes that, when organic life started, the Earth's surface was chemically more active than at present. He suggests that hydrogen sulfide might have been available to bacteria for the reduction of carbon dioxide, first in dark and then, with the advent of the purple bacteria, in light. The next stage in the evolution is the advent of the green plants, which reduce carbon dioxide in light by means of water. The transition from bacteria to algae, which were no longer dependent on the decreasing supply of hydrogen sulfide as a hydrogen donor, allowed life to spread over the whole surface of the Earth. During the further development of plant life, the first land plants appeared in the Silurian, and the first green forests were formed about $70 \cdot 10^6$ — $110 \cdot 10^6$ years ago in the Cretaceous and the Tertiary.

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A landmark in the development of animals is the appearance of the first calcareous skeletons in the Cambrian, about $500 \cdot 10^6$ years ago. The animals are now powerfully developed, and their formation is one of the most important processes in the evolution of the biosphere. The evolution of man started 15 or 20 million years ago. However, modern man did not appear until some 100,000 years ago, and the action of the anthroposphere as a powerful geochemical agent has been in process but a few hundred years.

With the formation of the biosphere, the foremost biophile elements have resumed an increasingly important role in reactions affecting the chemical composition of the three other uppermost geochemical spheres. According to Goldschmidt (1926, 1929, 1933*b*), the reactions between the biosphere, on the one hand, and the lithosphere, the hydrosphere, and the atmosphere, on the other hand, form the fourth stage in the geochemical differentiation of the Earth. Valence properties and physical principles dominate the reactions. The biochemical formation of free atmospheric oxygen is the most important process in the evolution of the atmosphere. A part of sedimentation takes place with the help of organisms, e.g., the deposition of the hydroxides of iron and manganese and, in particular, the deposition of calcium carbonate. The role of the biosphere is of high importance in the geochemistry of oxygen, carbon, nitrogen, and calcium and, in addition, in that of phosphorus and iodine. The manner of occurrence of these elements in the biosphere is discussed in the respective chapters in Part II of this book.

The geochemical activities of the anthroposphere were briefly discussed in chapter 8. Suffice it to state here that man is able to cause changes in the composition of all the outermost geochemical spheres of the Earth. So far it is unknown whether any of these changes disturb the balance of Nature. With special reference to the biosphere, it may be added that man is capable of increasing the mass of living matter, particularly the mass of plants, by regulating the productivity of soil.

PART II

MANNER OF OCCURRENCE OF THE ELEMENTS

INTRODUCTION

THE general principles governing the abundance of the elements and nuclides and their manner of occurrence were discussed in Part I of this book. The basis of the discussion was formed by the specifications presented in the introductory chapter dealing with the definition of geochemistry. Part II deals more specifically with the manner of occurrence and distribution of the elements in the three uppermost geospheres and, as far as possible, in the Earth's interior. The upper lithosphere, as governed by the geochemical laws and rules already presented, forms one of the most important subjects of this study.

If a survey of the geochemistry of an element is carried out, certain of its basic features must be explained and fundamental information concerning its manner of occurrence and distribution collected. According to the principles presented in the introductory chapters, the questions of essential importance for the geochemistry of an element are the following:

1. The manner of occurrence of the element in the geochemical spheres of the Earth
2. Its general geochemical character
3. Its manner of occurrence in mineral structures
4. Its course during the normal crystallization of magmas (endogenic differentiation)
5. Its role in the processes of decomposition, transportation, and redeposition of matter during the cycle of weathering (exogenic differentiation)
6. Its abundance, particularly in the uppermost part of the silicate crust of the Earth

In addition, the manner of occurrence and abundance of the element in meteorites is commonly discussed and, likewise, its role, if any, in metamorphic phenomena and its concentration in mineral deposits of economic importance.

All these questions dealing with the geochemical characterization of the elements have been already discussed in Part I of this book.

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However, the main emphasis was there laid on rules of general character, and the specific geochemical features of the elements were not examined. In the following chapters the general principles will receive less attention, whereas the individual geochemical character of each element will be emphasized.

HYDROGEN

ABUNDANCE AND GEOCHEMICAL CHARACTER

HYDROGEN is geochemically a lithophile, atmophile, and biophile element. Its cosmic abundance is high. Methane, in a large excess of hydrogen, is present in the atmospheres of the giant planets. In addition, small amounts of ammonia are found in the atmospheres of Jupiter and Saturn. Internally, the giant planets consist of a core surrounded by a layer of ice and another consisting of highly compressed hydrogen (see chap. 9). According to the values given in Table 2.3, the atomic abundance of hydrogen in the Sun's atmosphere is nearly nine hundred times as high as that of silicon and approximately thirty times as great as that of oxygen, since more than 80 per cent of the atoms in the solar atmosphere consists of hydrogen. Russell (1933) estimates that hydrogen in stellar atmospheres is about one thousand times as abundant as all the metals together. Hydrogen is the all-important source of stellar energy, which is released by the transmutation of protons into helium nuclei (see chap. 2). The abundance of hydrogen is probably less in stellar interiors than in stellar atmospheres. According to Biermann (1943), 55 per cent of the total mass of the Sun consists of hydrogen, whereas 34 per cent consists of carbon, nitrogen, oxygen, fluorine, and neon, 11 per cent of helium, and only about 0.5 per cent of metals. Unsöld (1947) found the H:He ratio in a solar prominence as 5:1, or similar to that present in many stars. The study of the star τ Scorpii by Unsöld (1941) gave the following composition by weight: hydrogen, 57 per cent; helium, 40 per cent; all other elements, 3 per cent. As in stellar atmospheres, hydrogen is by far the most abundant element in planetary nebulae and in interstellar space also. Hydrogen compounds are recorded in the spectra of comets and found among the gases contained in meteorites. It is evident that the cosmic abundance of hydrogen is very decidedly higher than its terrestrial abundance.

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The high cosmic abundance of hydrogen led Kuhn and Rittmann (1941) to the assumption that the Earth's interior, contrary to the commonly adopted views, does not consist of nickel-iron, being composed, instead, of undifferentiated solar matter, i.e., mainly of hydrogen (see chap. 3). According to this assumption, the content of hydrogen in the Earth's interior should be materially higher than in the surface layers, that is, in the lithosphere, hydrosphere, and atmosphere. However, the hypothesis of Kuhn and Rittmann is, so far, not generally accepted.

No figures were given in Table 2.3 for the content of hydrogen in igneous rocks and in meteorites. Although the amount of hydrogen present in the hydrosphere and atmosphere can be calculated—the hydrogen found in the hydrosphere constitutes approximately only 0.003 per cent of the Earth's mass—the estimation of the terrestrial abundance of hydrogen is associated with considerable difficulty (Goldschmidt, 1937*b*). The water in a magma is never totally contained in the primary results of magmatic crystallization, i.e., igneous rocks, but is removed, to a large extent, during the later stages of crystallization. Moreover, a part of the water present in igneous rocks is indisputably of secondary origin, being incorporated with the rocks in metamorphic phenomena of various kinds. This is true also in the case of unweathered- and unaltered-looking rocks. When analyzing minerals and rocks, two different water determinations are usually carried out, viz., that of combined water ($\text{H}_2\text{O}+$) and that of hygroscopic water ($\text{H}_2\text{O}-$). The latter escapes by heating to approximately 110°C ., whereas the former can be expelled only by heating well above this temperature. It is evident that $\text{H}_2\text{O}+$ is an essential constituent of the structures of minerals, being partly genuine magmatic water and partly of metamorphic origin, whereas $\text{H}_2\text{O}-$ is adherent hygroscopic moisture of secondary origin.

Up to 10 per cent water has been found in volcanic glass. The average H_2O percentage of igneous rocks, as given by Clarke and Washington (1924; see Table 2.1), is 1.15, and the corresponding percentage of hydrogen is 0.13. However, owing to reasons discussed above, this value cannot be used when estimating the abundance of hydrogen in igneous rocks. The conclusion follows that a satisfactory value of the abundance of this element in the upper lithosphere cannot be deduced. As to the meteorites, they contain almost no water, and only in rare instances are some of them found to carry hydrogen, both free and combined, to form methane and hydrogen sulfide.

HYDROGEN IN IGNEOUS ROCKS

During the magmatic differentiation, water and the other easily volatile compounds become notably enriched in the residual "melt" toward the end of the process. During the pegmatitic stage and, more especially, the pneumatolytic and hydrothermal stages, water is concentrated to such a degree that the residual melt has the character of an overheated aqueous solution. It is also known that during the early stages of crystallization the volatile constituents, particularly water, may affect the course of the process. As was pointed out in chapter 5, very great and extraordinarily small water content in a magma will pronouncedly change the course of crystallization, whereby the order of separation of the minerals from magma partly follows another course from that in the normal differentiation by crystallization.

The part of water which is not combined within the rocks during magmatic differentiation is separated out from the magma and wells as the main constituent in volcanic emanations, making up as much as nearly a hundred per cent of the volume of the fumarole gases. The volcanic emanations contain, in addition, other hydrogen compounds. According to Zies (1929), the steam emitted in 1919 by the fumaroles in the Valley of Ten Thousand Smokes in Alaska contained, on an average, 0.117 per cent (by volume) HCl, 0.032 per cent HF, and 0.029 per cent H₂S. Here considerable surface water was added to the emanations as steam, and the average percentage, by volume, of water vapor in the fumarolic gas was 99.65.

No calculations have been carried out dealing with the proportion of the original water content of magmas remaining in primary igneous rocks. The amount set free by volcanic emanations is accordingly not known with any definite certainty. At any rate, it is evident that during the geological history of the Earth the juvenile waters have provided a certain increment to the water in the hydrosphere. However, the estimates concerning the amount of juvenile water are rather uncertain, and the conclusion is apparent that no reliable value can be given to show the amount of water in the upper geochemical spheres of the Earth.

Hydrogen is found to be combined in the mineral structures in four basically different ways:

1. Hydrogen is combined with oxygen to form independent hydroxyl groups. The radius of the OH⁻ ion is similar to that of the

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O^{2-} ion because the H^+ ion does not possess electrons and consequently needs practically no space in the structure. As was presented in chapter 5, the bond depends on the polarization of the cation, being either ionic bond or covalent hydroxyl bond or hydrogen bond. In any case the OH^- ion forms an essential constituent of the structure, and it cannot be removed without the collapse of the structure. The structures of the amphiboles and the micas are given as examples of this group (see Figs. 5.8 and 5.14).

2. Hydrogen is combined with oxygen to form water molecules. These are, as such, independent constituents of the structure. Like other such constituents, they occupy well-determined structural positions and consequently cannot be removed without breaking down the structure. Gypsum, $Ca[SO_4] \cdot 2H_2O$, is an example of this group.

3. The water molecules are only loosely combined within the structure and may be removed by heating, without damage to the structure. The water molecules occupy more or less fixed positions in the structure, not, however, being essential to its existence. The zeolites and montmorillonite afford examples of this group (see Fig. 5.18).

4. Hydrogen occurs as independent H^+ and H^- ions. The former are found, for example, in certain salt minerals, and the latter occur in hydrides. This manner of occurrence of hydrogen is quantitatively of minor importance as far as the upper lithosphere is considered. However, the hydrides may perhaps have played a role during the early stages of the geochemical evolution of the Earth.

The rocks also contain hydrogen as water in inclusions and in their pore space.

HYDROGEN AND ITS CYCLE IN THE HYDROSPHERE AND ATMOSPHERE

By far the greatest part of hydrogen present in the outermost geospheres occurs as water in the hydrosphere. Water and ice are, as a matter of fact, the only important hydrogen minerals. Compared with water, all other occurrences of hydrogen are rather unimportant. A conservative estimate by Goranson (1931) of the amount of water in the oceans, seas, on the land surface, and bound up in surface rocks gives $1.64 \cdot 10^{18}$ tons, or 16,400 Gg. The free hydrogen released by volcanic emanations and produced in the biosphere, as well as the other hydrogen-bearing constituents of the atmosphere, such as hydrogen peroxide, methane, and ammonia, are of minor importance in the geochemistry of this element.

Water plays the most important role in the geochemistry of hydrogen. The cycle of water was discussed by Meinardus (1928). There exists a continual exchange of water between the atmosphere, the surface of the Earth, and the hydrosphere. The water may evaporate from the sea and return thereto as rain water; it may evaporate from the land surface and return as precipitation; or it may evaporate from the sea, fall as rain on the land surface, and return to the sea as surface water. The cycle of water is of high geochemical importance because it is part of the processes of weathering, transportation, and redeposition of matter on the Earth's surface and because water also forms the fluid phase in which the deposition of matter takes place (see chaps. 5, 6, and 7). In addition, water as such or activated by dissolved substances attacks minerals chemically and decomposes them. According to Goldschmidt (1933, 1937*b*), the total water content of the hydrosphere is 282.7 kg per square centimeter of the Earth's surface. During the geological history of the Earth, 160 kg·cm⁻² igneous, sedimentary, and metamorphic rocks have been weathered, with the resulting formation of 155 kg·cm⁻² resistates and hydrolyzates. Much water is bound within these sediments during their formation. Goldschmidt estimates this amount as approximately 6 kg·cm⁻², which corresponds to about 2.2 per cent of the total quantity of water in the hydrosphere. It is thus evident that notable amounts of water are transferred during the disintegration of rocks and the formation of sediments into the products generated; and this phenomenon counteracts the volcanic emanations, which work toward the increase of the quantity of water in the hydrosphere. Some water is also liberated during the solution of hydrous minerals, e.g., gypsum, and in some metamorphic processes. Whether or not these two opposite processes counterbalance each other, i.e., whether there is an increase or a decrease in the amount of water in the hydrosphere, is a question which cannot, so far, be definitely answered. According to the opinion of Goldschmidt (1937*b*), the present hydrosphere was formed mainly during the geological history of the Earth, and the amount of juvenile water given off by magmas is notably in excess over the amount of water bound during weathering and water-consuming metamorphic processes. Consequently, the quantity of water in the hydrosphere will gradually increase (see also chap. 10).

“ The hydrogen ion, H⁺, the most electropositive and mobile of all ions, is present in all aqueous solutions. Geochemically, the most im-

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portant property of water is the fact that all salts dissolved in water are dissociated into ions. The presence of water also causes certain metals to occur in the native state during their exogenic cycle, whereas other metals react with water and become separated from aqueous solutions in the form of hydroxides, oxides, or sulfides. A measure of this property is the normal potential of the metal in question.

The affinity of hydrogen for oxygen is very high. Consequently, the amount of free hydrogen in the atmosphere is kept small. The low density of hydrogen, in addition, is responsible for the migration of hydrogen toward the upper layers of the atmosphere, where it, like helium, is removed by dissipation into the interplanetary space (Russell and Menzel, 1933; see chap. 7). Thus the hydrogen produced by the volcanoes and in the biochemical processes is removed from the atmosphere, unless it is combined with oxygen by electrical discharges and forms water on the lower levels in the atmosphere. It is probable that during the earlier stages of the evolution of the Earth the primordial atmosphere contained more hydrogen than the present one does. This primary hydrogen, however, has evidently long since escaped from the gravitational field of the Earth.

HYDROGEN IN THE BIOSPHERE

The pronouncedly biophile character of hydrogen is displayed in the fact that this element is inferior only to oxygen and nitrogen in biological importance. Free hydrogen is formed as an end-product of cellulose fermentation, but this process seems to be the only instance in which molecular hydrogen enters the more important biological processes. Water makes up 60–80 per cent of all tissues. Hydrogen peroxide, H_2O_2 , is found as an intermediate reactant in biological systems, and ammonia, NH_3 , is of importance in the biological cycle of nitrogen.

Hydrogen in various organic compounds is present in all organic systems existing in the biosphere and in most bioliths. Petroleum and natural gas are the most important hydrogen-bearing sediments belonging to this class. They were discussed in chapter 8.

DEUTERIUM

The heavy isotope of hydrogen, deuterium, has an average terrestrial abundance of 0.02 per cent against the percentage of 99.98 of the light isotope. The presence of deuterium has not been established in

the Sun, and hence its solar abundance must be very low. As to the Earth, deuterium is believed to concentrate in natural gas and petroleum hydrocarbons. The variations in the density of natural waters are due both to the variations in the content of the oxygen isotopes O^{16} , O^{17} , and O^{18} and to the variations in the hydrogen isotopes. However, according to Wirth, Thompson, and Utterback (1935), deuterium oxide is relatively enriched in the surface layers of the sea, owing to evaporation of sea water, and the density of sea water is somewhat higher than that of fresh water (see chap. 27).

THE ALKALI METALS: LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CESIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

THE five alkali metals have stable isotopes which occur in Nature. Francium (AcK), with the atomic number 87, is known only as an unstable disintegration product of actinium (see chap. 46). The alkali metals form a chemically rather coherent group in the Periodic System, and in this respect they differ from many other groups of elements. The uniform valence of the alkali metals, all of which form univalent positive ions; the strongly basic nature of their hydroxides; and the ready solubility and volatility of most of their compounds are properties which are either totally absent in other groups of elements or, if present, are displayed by only a few members of such groups.

Two of the alkali metals, viz., sodium and potassium, belong to the main constituents of the upper lithosphere. Rubidium is one of the most abundant trace elements therein, but lithium and particularly cesium are rare. Like its neighbors in the Periodic System, beryllium and boron, lithium is scarce in cosmic matter also (see chap. 2).

The abundance of the alkali metals is presented in Table 12.1. Although no direct determinations are at hand, the content of the alkali metals in the meteoritic irons and in troilites must be negligible. The values recorded in Table 12.1 are from the following sources: Li in silicate meteorites, Rb and Cs in igneous rocks from Goldschmidt (1937*b*); Na and K in silicate meteorites from Merrill (1916), recalculated by Goldschmidt (1937*b*); Rb and Cs in silicate meteorites from Noddack and Noddack (1930); Li in igneous rocks from Strock (1936); Na and K in igneous rocks from Clarke and Washington (1924).

A determination of the average lithium content of igneous rocks by L  ndeg  rdh (1946) gave 60 g/ton, in full agreement with the value given in Table 12.1.

As regards their general geochemical character, the alkali metals are very strongly lithophile. In the Earth they are evidently almost completely absent in the inner geochemical shells. In the lithosphere they are strongly enriched in the Sial crust, and they are all pronouncedly oxyphile. In the Sima layer their content is considerably lower than in the Sial crust, as may be concluded from the analyses of silicate meteorites.

Along with their absolute abundance, their relative abundance also varies in the different layers of the lithosphere. The values given in Table 12.1 show that the Na:K ratio in igneous rocks is 1.09:1, whereas in the silicate meteorites the ratio is 3.85:1. Consequently, the Sima layer, the closest counterpart of which are the silicate mete-

TABLE 12.1
ABUNDANCE OF ALKALI METALS

MATERIAL	Li	Na	K	Rb	Cs
	g/ton				
Iron phase of the meteorites	unknown	unknown	unknown	unknown	unknown
Sulfide phase of the meteorites	unknown	unknown	unknown	unknown	unknown
Silicate phase of the meteorites	5	7,700	2,000	4 5	0.1
Igneous rocks.....	65	28,300	25,900	310	7

orites, contains, on an average, nearly four times as much sodium as do the igneous rocks, i.e., potassium is impoverished by a factor of 4. Also lithium, rubidium, and cesium show a similar impoverishment, and the effect is most pronounced in the case of rubidium.

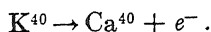
The alkali metals, with the exception of cesium, are present in the solar atmosphere.

The potassium isotope, K^{40} , and the rubidium isotope, Rb^{87} , are radioactive. The former is the least abundant of the three potassium isotopes; its abundance is only 0.012 per cent. The rubidium isotope is rather abundant (27.2 per cent) and has a half-life of $6.3 \cdot 10^{10}$ years and decays into Sr^{87} (see chap. 15). No significant differences are found in the K^{40} content of potassium from animal, vegetable, and mineral sources. Likewise, there is no material difference in the proportion of K^{40} in terrestrial and meteoritic potassium (Schumb, Evans, and Leaders, 1941).

The isotope K^{40} has two stable isobars, viz., A^{40} and Ca^{40} . The de-

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cay into Ca^{40} explains the normal β -activity of K^{40} . Electrons are released in this process, as follows:



The production of A^{40} from K^{40} is also possible, but, according to Suess (1948), it is most likely that only 0.5–10 per cent of the decaying K^{40} is converted into argon. In any case the high abundance of A^{40} in the atmosphere is the result of the decay of K^{40} (see chap. 45).

Cook (1943), in a study dealing with the $\text{K}^{39}:\text{K}^{41}$ ratio in certain Pacific seaweeds, fossils, and rocks of different geological age, did not find any measurable differences in the potassium isotope ratio.

TABLE 12.2
CONTENT OF LITHIUM IN IGNEOUS ROCKS

Rock	Li (g/ton)
Dunite, eclogite (Strock, 1936)	2.3
Anorthosite (Strock, 1936)	0.9
Pyroxenite (Strock, 1936)	0.7
Traps, Deccan, composite (Strock, 1936)	7.4
Gabbros, Germany, composite (Strock, 1936)	9.7
Andesites, composite (Strock, 1936)	15.2
Granites, Germany, composite (Strock, 1936)	179.4
Granites, Saxony (connected with pneumatolytic activity), composite (Strock, 1936)	460–690
Greisen rocks, Erzgebirge, Germany, composite (Goldschmidt, Berman, Hauptmann, and Peters, 1933)	1,380
Liparites, Italy, composite (Strock, 1936)	33.6
Nepheline syenites, composite (Strock, 1936)	23.5
Phonolites, composite (Strock, 1936)	31.7
Basic rocks (Lundegårdh, 1946)	75
Acidic rocks (Lundegårdh, 1946)	70

LITHIUM IN IGNEOUS ROCKS

The lithium content of the various classes of igneous rocks is presented in Table 12.2. The values show that lithium tends to become enriched in the latest products formed during the crystallization of a magma, particularly in granitic rocks. However, the degree of enrichment does not increase regularly as, for example, in the case of sodium. The granites contain around one hundred times as much lithium as do the early crystallates. Lithium is enriched also in syenites and nepheline syenites, but in these rocks the degree of enrichment is lower than in the granites. Magmatic sulfides are totally devoid of lithium.

In a certain respect lithium departs very pronouncedly from the other alkali metals, viz., in its reluctance to enter the feldspar struc-

tures. The potash feldspars and the plagioclases formed during the main stage of crystallization usually are devoid of lithium, and, in spite of the fact that this metal often forms independent minerals in pegmatites, it has never been found to form a feldspar therein. Ahrens (1945) found that a content higher than 5 g/ton Li in a feldspar is exceptional; but Hess (1940) reports as much as 1.2 per cent Li in microcline from spodumene pegmatites.

The distribution of lithium among the various rock-making minerals is illustrated by an analysis of ditroite and its minerals (Strock, 1936), given in Table 12.3. The values presented therein show that the light constituents, viz., the feldspars, nepheline, etc., are very poor in lithium and that it is enriched in the dark constituents, which is the general rule governing the distribution of lithium in the minerals of igneous rocks. Schiebold (1931) has shown that lithium, for

TABLE 12.3
CONTENT OF LITHIUM IN DITROITE FROM BRATHOLMEN,
NORWAY, AND IN ITS MINERALS

Material	Li (g/ton)
Ditroite	506
Light constituents (90 per cent of the rock) . . .	46
Mica (5 per cent of the rock)	2,300
Amphibole and pyroxene (5 per cent of the rock)	1,610

thermochemical reasons, cannot form a feldspar structure. If the chemical composition of a lithium-bearing melt or solution allows the formation of a lithium feldspar during the crystallization, the lithium pyroxene spodumene, $\text{LiAl}[\text{Si}_2\text{O}_6]$, or petalite, $(\text{Li}, \text{Na})[\text{AlSi}_4\text{O}_{10}]$, will crystallize instead. The former resembles feldspars in composition, but the latter is a tectosilicate, which, however, differs from the feldspars in its structure.

Lundegårdh (1946) suggests that Li^+ is able to replace Al^{3+} in the plagioclase structure.

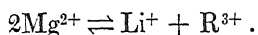
With reference to the co-ordination number, lithium differs totally from the other alkali metals. In lithium micas the Li^+ ion does not occupy a structural position similar to that of the K^+ ion (see chap. 5) but replaces Al^{3+} and Mg^{2+} in the structure. In spodumene, $\text{LiAl}[\text{Si}_2\text{O}_6]$, lithium forms $[\text{LiO}_6]$ groups, being thus 6-co-ordinated, whereas in diopside, $\text{CaMg}[\text{Si}_2\text{O}_6]$, the corresponding Ca-O group is $[\text{CaO}_8]$. In cryolithionite, $\text{Na}_3\text{Al}_2[\text{LiF}_4]_3$, the co-ordination number of lithium is 4.

According to Landergren (1948), most pre-Cambrian iron ores and

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associated rocks in Sweden show a strong deficiency in lithium. This is a very remarkable observation because it would be reasonable to assume that Li^+ , which replaces Mg^{2+} in femic minerals, would be enriched in these ores, which are rich in both magnesium and iron. Landergren uses this result to show that the iron ores of central Sweden cannot be of primary igneous origin.

The strong enrichment of lithium in micas, amphiboles, and pyroxenes during the course of the crystallization of a magma must be emphasized. As pointed out above, Li^+ (radius 0.78 kX) replaces Mg^{2+} (radius 0.78 kX) in minerals; both ions are 6-co-ordinated in silicate structures. Thus magnesium, because of its high abundance, acts as the protective element of lithium. Strock (1936) suggested that the replacement is possible only when the electrical balance of the structure is maintained by the introduction of a trivalent 6-co-ordinated cation, according to the equation



Among the trivalent cations, only Fe^{3+} is sufficiently abundant in rocks and is consequently introduced into the structure. Strock explained the increase in the lithium content during the progressive differentiation as a result of the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio. However, as pointed out by Wickman (1943), the Fe^{3+} content does not materially change during the differentiation, because the Fe^{3+} ion is so immobile that it will become incorporated in a suitable mineral structure under any conditions. On the other hand, the Fe^{2+} content decreases during the differentiation, partly owing to oxidation to Fe^{3+} , and this process is mainly responsible for the change in the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio. The E -value of Li^+ is small, evidently much smaller than that of Mg^{2+} , and therefore lithium is incorporated in the structures at high temperatures only in a limited quantity; but with decreasing temperature an increasing amount of Li^+ ions becomes sufficiently immobile to participate in crystallization.

Another point of importance is that during the replacement of Mg^{2+} by Li^+ the structure suffers a loss in energy. When the Li^+ ion with a lower charge than Mg^{2+} is admitted, the bonds in the structure become weakened. Therefore, no considerable replacement can take place until a relatively low temperature has been reached, i.e., toward the later steps in the main stage of crystallization. It is thus evident that the dark magnesium minerals of the granites, especially the

micas, will be the richest in lithium. It has long been known that lithium-rich micas occur in greisen and in granite pegmatites. Hess (1940) reports 0.4 per cent Li in muscovite and 0.5 per cent in biotite from a granite in the neighborhood of spodumene pegmatites in North Carolina in the United States. Biotite in the country rock (schist) penetrated by the pegmatites contains 1.5 per cent Li. The average content of lithium in micas is presented in Table 12.7.

In nepheline syenites, lithium is also contained in the salic sodium-bearing silicate minerals, particularly in nepheline. In the nepheline syenite minerals the enrichment of lithium is less pronounced than in the minerals of the granites. Among the dark constituents of basic rocks the orthorhombic pyroxenes, according to Strock (1936), are low in lithium, whereas in the monoclinic pyroxenes the content is higher, and probably still higher in amphiboles. The lithium content of monoclinic pyroxenes increases continually during the course of differentiation, along with the decrease in Mg^{2+} and the increase in Fe^{2+} in these minerals. Lundegårdh (1946), however, concludes that the Li content is not a function of the Mg content; and, according to Landergren (1948), Strock's conclusions are valid only in pure fractional crystallization when no external material has been added.

Lithium, along with fluorine, chlorine, phosphorus, and manganese, is often enriched so strongly in granite and nepheline syenite pegmatites that it forms independent minerals. These minerals include cryolithionite, $Na_3Al_2[LiF_4]_3$; triphylite, $Li(Fe^{2+}, Mn^{2+})[PO_4]$; lithiophilite, $Li(Mn^{2+}, Fe^{2+})[PO_4]$; amblygonite, $LiAl[(F, OH) | PO_4]$; petalite, $(Li, Na)[AlSi_4O_{10}]$; spodumene, $LiAl[Si_2O_6]$, and its alteration product, eucryptite, $Li[AlSiO_4]$; the lithium micas lepidolite, zinnwaldite, and cookeite; lithium tourmaline; the very rare lithium amphibole holmquistite; and still others. The pegmatite minerals amblygonite (8–10 per cent Li_2O), spodumene (4.5–7.5 per cent Li_2O), and lepidolite (3–10 per cent Li_2O) are an important industrial source of lithium; but more than half the world's total lithium supply is obtained from Searles Lake in California in the United States (see chap. 6).

According to Bjørlykke (1937), the absence of lithium is characteristic of Norwegian granite pegmatites. This observation affords proof of the regional behavior of lithium.

The minerals which crystallize from late hydrothermal solutions, e.g., zeolites, are usually low in lithium.

CYCLE OF LITHIUM

In the processes of weathering and sedimentation lithium follows the course of magnesium. The geochemical balances presented in Table 6.19 show that lithium, unlike sodium, is incorporated in marine hydrolyzate sediments. The Li:Mg ratio in hydrolyzates, marine oxidates, and limestones is of approximately the same magnitude as in igneous rocks. In sea water the ratio is different:

	Li:Mg
Igneous rocks	0.0034
Sea water	0.00008

The above values are based on those presented in Tables 2.3 and 6.17. They show that in sea water the degree of impoverishment of lithium in regard to magnesium is about forty-three times. This ought to

TABLE 12.4
CONTENT OF LITHIUM IN SEDIMENTS AND THEIR DERIVATIVES

Material	Li (g/ton)
Sandstones (calculated from Strock, 1936)	17
Laterite-bauxite ores (Landergren, 1948)	<5
Bog iron ores, Finland (Landergren, 1948)	10
Shales (calculated from Strock, 1936)	46
Marine oolitic-siliceous iron ores (Landergren, 1948)	120
Marine siderite ores (Landergren, 1948)	100
Red clay (Strock, 1936)	78
Manganese nodule (Strock, 1936)	55
Glauconite (Strock, 1936)	161
Limestones, minimum (calculated from Strock, 1936)	26

imply a corresponding enrichment of lithium in marine hydrolyzates, contrary to the behavior of magnesium. However, only insignificant amounts of salts are dissolved in sea water, compared with the grand total of sediments, and therefore the enrichment of lithium cannot be very considerable. Some lithium is present in evaporate sediments, e.g., in halite, in which it replaces sodium in small quantities.

The content of lithium in sediments and their derivatives is presented by the analyses in Table 12.4. The values show that in marine iron ores and in deep-sea sediments the content of lithium is higher than the average content in hydrolyzates.

Thermal waters often contain notable quantities of lithium, leached out as the easily soluble chloride, LiCl, from rocks penetrated by the waters. The origin of this metal is similar in mineral waters, which carry it as a frequent constituent.

In metamorphic processes lithium seems to follow magnesium.

SODIUM AND POTASSIUM IN IGNEOUS ROCKS

With the exception of villiaumite, NaF, which is found only in the cavities of nepheline syenite from the Los Archipelago in French Guinea, the alkali metals do not form any simple compounds in igneous rocks. They are present only in complex compounds, formed together with other metals. This fact is caused by the high solubility of their simple salts. Sodium and potassium occur only as univalent cations with radii of 0.98 and 1.33 kX, respectively. Consequently, they require considerable space in mineral structures. The co-ordination numbers of these cations are therefore necessarily high, and the interatomic forces binding sodium and potassium in mineral structures cannot be very strong. Their E -values are low, and consequently they become readily enriched in residual melts and solutions during the magmatic differentiation. All alkali metals are either totally absent in the early crystallates or present only in small amounts.

The average mineralogical composition of igneous rocks must be considered, in order to comprehend fully the manner of distribution of sodium and potassium therein. According to Clarke (1924; see Table 5.16), about 60 per cent of the minerals of igneous rocks consist of feldspars. Because the minerals of this group either are pure alkali feldspars or nearly always contain varying amounts of the alkali components, the bulk of sodium and potassium in igneous rocks must be found in the feldspars.

Among the alkali feldspars, the potash feldspars, $K[AlSi_3O_8]$, are minerals peculiar to the last steps of the main stage of crystallization. In addition, they are characteristic of the late crystallates. According to the conditions prevailing during crystallization, there occurs either the triclinic form (microcline) or the monoclinic ones (orthoclase, sanidine, adularia). In a normal differentiation series considerable amounts of potash feldspar are not present until in granitic rocks. Only during the crystallization of very dry melts is potash feldspar formed during the earlier steps of the main stage. The soda feldspar albite, $Na[AlSi_3O_8]$, on the other hand, has already begun to separate at the beginning of the main stage of crystallization as isomorphic mixtures with anorthite (the plagioclase feldspars). The formation of plagioclase still continues during the late stages of crystallization. However, the composition of plagioclase changes gradually during the differentiation from labradorite, which is rich in the anorthite

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component, to oligoclase, rich in the albite component. The content of sodium reaches a maximum in granites and nepheline syenites. This is the principal reason for the change in the Na:K ratio during the main stage of crystallization. The content of potassium increases in relation to sodium, as is shown by the Na:K ratios, calculated from Daly's (1933) averages (see Table 5.32), given in the accompanying tabulation.

Rock	Na:K
Gabbros	2.55
Diorites	1.43
Granodiorites	1.20
Granites	0.76

In alkalic rocks potassium and sodium are present both in feldspars and in feldspathoids, especially in nepheline, $\text{Na}[\text{AlSiO}_4]$, and leucite, $\beta\text{-K}[\text{AlSi}_2\text{O}_6]$. They are also found as constituents of the alkali pyroxenes and alkali amphiboles, and a number of complex titanium and zirconium silicates (see chap. 21), but the geochemical significance of these minerals is small. Sodium is the more important of these alkali metals in the alkali amphiboles and pyroxenes. It is incorporated in these minerals if there is a definite excess of sodium over aluminum, and, consequently, all sodium does not become introduced into the feldspars. The greater ionic radius of potassium prevents the incorporation of notable amounts of this metal in the amphibole and pyroxene structures.

Along with the feldspars and feldspathoids, the micas are important carriers of sodium and potassium in igneous rocks. According to Clarke (1924; Table 5.16), the average content of biotite in igneous rocks is 3.8 per cent. The analyses of Chirvinsky (Table 5.28) show that the average content of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ in muscovite from granites is 11.79 per cent and in biotite from like rocks, 9.14 per cent. Consequently, notable amounts of the alkalies are found in the micas. There is, however, a geochemically important difference between the manner of occurrence of sodium and potassium in feldspars and in micas. In the feldspar group soda feldspar is about as abundant as potash feldspar. In the mica group, on the contrary, the sodium mica (paragonite) is comparatively rare and therefore does not have much geochemical importance. All common and important micas are potassium minerals. Among them, biotite and muscovite belong to the main constituents of igneous rocks. They are formed chiefly during the last steps of the main stage of crystallization and occur also

among the late crystallates. However, biotite may form at an earlier stage if the water content of the magma is very high.

Sodium and potassium also occur in igneous rocks in a large number of minerals of minor geochemical importance. Some more notable species are cryolite, $\text{Na}_3[\text{AlF}_6]$; a number of halogenides also containing other cations; the minerals of the scapolite group; and the various zeolites.

CYCLE OF SODIUM AND POTASSIUM

During the weathering, some silicate minerals, for example, the alkali feldspars, leucite, and actinolite, are completely dissolved. Sodium and potassium released during the weathering remain in ionic solution, whereas aluminum reacts with silica to form clay minerals, and also perhaps to form muscovite with a part of the potassium. The weathering of the micas may be different: often only potassium is extracted from the structure, but a small part of it remains in the aluminosilicate framework, from which the clay minerals in the hydrolyzate sediments are built up. Sodium and potassium are carried into the sea by rivers and streams. They may remain in the weathering residue only in arid regions.

During their cycles sodium and potassium, however, follow different courses. The differences in their behavior during the migration are illustrated by the values presented in Table 12.5. The percentages are taken or calculated from Tables 2.3 and 6.7 and from Clarke (1924; Table 5.52).

Because sodium is extracted from rocks during the weathering, its absolute amount decreases in the hydrolyzate sediments which are formed as the result of chemical decomposition. Potassium, on the other hand, goes first into solution but does not remain dissolved: it is largely adsorbed by, and even enriched in, clays, as the Na:K ratios of Table 12.5 show. It has also been suggested that the difference in the behavior of sodium and potassium during the weathering is caused by the greater resistance of potash feldspar as compared with that of the plagioclase feldspar, which causes an initial accumulation of potassium (and barium) in potash feldspar during the decomposition of plagioclase. The explanation has further been offered that much potassium is utilized by plants and thus removed from the cycle in the form of relatively insoluble organic compounds. However, the separation of sodium and potassium during weathering also takes place without plants, and therefore the sorption phenomena

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evidently are the most important factor of separation during the later stages of weathering and the accumulation of sediments.

In igneous rocks the average content of sodium is somewhat higher than that of potassium, but the difference is small. In lake and river waters, which are the first link in the journey of the dissolved salts toward the sea, potassium is already notably impoverished in regard to sodium. In sea water only a small part of the originally dissolved potassium remains in solution, which now shows a strong predominance of sodium. It is thus evident that the adsorption of potassium in clays or the formation of new potassium-bearing mica-like minerals starts as soon as this metal goes into solution during the weathering. The adsorption is completed in the sea. Table 12.5 shows that

TABLE 12.5
CONTENT OF SODIUM AND POTASSIUM AND THE
Na:K RATIO IN THE MINOR CYCLE

MATERIAL	Na	K	Na:K
	Per Cent		
Igneous rocks.	2 83	2 59	1 09
Dissolved solids in lake and river water	5 79	2 12	2.73
Dissolved solids in sea water	30 62	1 10	27 84
Argillaceous sediments (shales)	0 97	2 70	0 36

potassium predominates over sodium in argillaceous sediments. Potassium, with a greater ionic radius and a lower ionic potential than sodium, will also become adsorbed by colloidal manganese hydroxide. This fact explains the presence of potassium in many manganese-rich oxidates and in secondary manganese minerals (see chap. 31).

The geochemical balances calculated in Table 6.19 show that only sodium, among the alkali metals, is thalassophile.

The content of potassium in sea water is also affected by dilution with river water and by biological activity. Some marine organisms, particularly the large algae, accumulate potassium. Further changes are caused by reactions taking place between sea water and fine-grained detrital minerals, colloid particles, and clay minerals (halmyrolysis). Some potassium is incorporated in glauconite and other potassium-bearing minerals, e.g., phillipsite and other zeolites formed in the bottom deposits. The formation of glauconite is referred to diagenetic changes of biotite (Galliher, 1939) or other parent-substances, among others, organic matter (e.g., Takahashi, 1939).

As a result of weathering, transportation, and adsorption, the grand total of sodium now present in the sea is 62 per cent of the total quantity transported thereto during the geological evolution of the Earth. The corresponding percentage for potassium is only 2.4 (see Table 6.19). Conway (1945) calculated that about 108 Gg potassium have been brought into the ocean by rivers during the geological history of the Earth. Of this amount, about 100 Gg have been removed in silicates, probably mainly in illite but also in glauconite and authigenic orthoclase. Conway (1943, 1945, 1947) also suggested that the rate of removal of potassium from the ocean has not been uniform but reached a peak in or near the late pre-Cambrian. He assigned the major role in the removal to illite but thought that after the Cambrian the removal by glauconite became increasingly significant and was dominant from the Mesozoic era onward. Conway (1947) further attributed the selective removal in illite to the fact that, among the four major hydrated cations (Mg^{2+} , Ca^{2+} , Na^+ , K^+) in the ocean, potassium is the smallest, being the least hydrated. Such size differences, according to Conway, determine the relative rates of entrance of K^+ and Na^+ into cells and also the fact that K^+ becomes concentrated therein, whereas Na^+ circulates in the extracellular fluids. The process of potassium fixation in the marine hydrolyzates releases an equivalent amount of H^+ ions, which have stabilized the pH of the ocean over a large fraction of its history.

The transfer percentage of sodium shows that the bulk of all sodium dissolved during weathering accumulates in the ocean, where it will remain for long periods of geological time. This fact has led to the assumption that the salt content of ocean water has gradually increased, inasmuch as the dissolved solids consist chiefly of sodium chloride. The present salinity of the ocean is approximately 35 parts per thousand, but it is evident that lower values existed during the earlier periods of the Earth's history. Some authorities have used this assumption to calculate the grand total of igneous and metamorphic rocks which have weathered during the history of the Earth and the amount of the sediments formed by their disintegration. The calculations made by Goldschmidt (1933a) were presented in chapter 5.

SODIUM AND POTASSIUM IN THE EVAPORATES

Goldschmidt's (1933) calculations dealing with the quantitative aspects of weathering and deposition (see chap. 5) do not consider the fact that part of the sodium originally transported into the sea has

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been lost in the formation of evaporate sediments. The formation of evaporates also accounts for the further decrease of the content of potassium in sea water. However, the quantitative effect of this factor on the calculations in question is not readily estimated. The quantity of sodium now present in sea water is known rather precisely, but no reliable estimate is available on the amount of sodium and potassium incorporated in the evaporates. The grand total of the evaporate sediments has never been calculated, and their average sodium and potassium content is not known with any reasonable certainty. However, Goldschmidt (1933) thinks that the factor discussed is quantitatively of minor importance and thus cannot substantially affect the calculations.

It is reasonable to assume that only a small part of all sodium and potassium transported into the ocean is now incorporated in the evaporate sediments. This part, even though small, is characteristic of the geochemistry of these metals. In addition, the evaporates and the concentrated brines of salt lakes are of high technical significance because they are the only important industrial sources of sodium and potassium. Some sodium chloride is also recovered by evaporating sea water.

The most important salt minerals of sodium and potassium which seem to be capable of crystallizing directly from sea water are the following:

1. SODIUM MINERALS

Glauberite,	$\text{Na}_2\text{Ca}[\text{SO}_4]_2$
Loeweite,	$\text{Na}_2\text{Mg}[\text{SO}_4]_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$
Astrakanite (blödite),	$\text{Na}_2\text{Mg}[\text{SO}_4]_2 \cdot 4\text{H}_2\text{O}$
Vanthoffite,	$\text{Na}_6\text{Mg}[\text{SO}_4]_4$
Mirabilite,	$\text{Na}_2[\text{SO}_4] \cdot 10\text{H}_2\text{O}$
Thenardite,	$\text{Na}_2[\text{SO}_4]$
Halite,	NaCl
Tychite,	$\text{Na}_6\text{Mg}_2[\text{SO}_4](\text{CO}_3)_4]$

2. POTASSIUM MINERALS

Polyhalite,	$\text{K}_2\text{Ca}_2\text{Mg}[\text{SO}_4]_4 \cdot 2\text{H}_2\text{O}$
Syngenite,	$\text{K}_2\text{Ca}[\text{SO}_4]_2 \cdot \text{H}_2\text{O}$
Schönite (picromerite),	$\text{K}_2\text{Mg}[\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$
Langbeinite,	$\text{K}_2\text{Mg}_2[\text{SO}_4]_3$
Leonite (potassium astrakanite),	$\text{K}_2\text{Mg}[\text{SO}_4]_2 \cdot 4\text{H}_2\text{O}$
Carnallite,	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Sylvite,	KCl
Kainite,	$\text{KMg}[\text{Cl} \text{SO}_4] \cdot 3\text{H}_2\text{O}$

3. SODIUM-POTASSIUM MINERALS

Glaserite (aphthitalite),	$\text{NaK}_3[\text{SO}_4]_2$
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The borate minerals of sodium and potassium which crystallize from closed basins are discussed in chapter 16 and the nitrate minerals in chapter 23.

The marine evaporate minerals listed above are either sodium or potassium salts or double salts containing these metals. There are no salt minerals which show a notable degree of diadochic replacement of sodium by potassium, or vice versa. The pure potassium salt minerals are remarkably poor in sodium, and the sodium minerals, as a rule, contain very little potassium. Thus the case is the opposite of that met in the silicate minerals of igneous rocks, in which these metals, notwithstanding the difference in their ionic size, afford examples of a distinct, even though limited, diadochic substitution.

The contrast between the behavior of sodium and that of potassium in the salt minerals and in igneous rocks is evidently due to the different temperatures at which the crystallization took place. At elevated temperatures the crystal structures expand, and the differences in the ionic dimensions do not restrict the possibility of diadochic replacement as much as they do at lower temperatures, at which the structures are more rigid. Petrological evidence and laboratory experiments afford ample proof of the ready miscibility of certain components at high temperatures. Because the primary saline minerals of the evaporates have crystallized at rather low temperatures, the lack of the diadochic replacement between sodium and potassium in their structures becomes evident.

Potassium and magnesium are typical of salt deposits of marine origin, particularly of those formed during the last stage of crystallization. The evaporates of continental origin, on the other hand, contain little or no potassium, and sodium predominates therein. Along with mirabilite, thenardite, and halite, the continental evaporates contain gaylussite, $\text{Na}_2\text{Ca}[\text{CO}_3]_2 \cdot 5\text{H}_2\text{O}$, and trona, $\text{Na}_3\text{H}[\text{CO}_3]_2 \cdot 2\text{H}_2\text{O}$. Thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$; natron, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; and pirssonite, $\text{Na}_2\text{Ca}[\text{CO}_3]_2 \cdot 2\text{H}_2\text{O}$, are also met in deposits of soda lakes. During the crystallization of salts from the brines of salt lakes, gaylussite is the first mineral to separate. Along with pirssonite, it contains all the calcium present in the brines. Trona is the next mineral to crystallize under ordinary conditions. It is of technical importance in the North American continental evaporates. The separation of sodium sulfate starts after the crystallization of trona. Warm brines deposit thenardite, whereas mirabilite crystallizes at lower temperatures. Halite is deposited after the separation

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of sodium sulfate, and the final stage consists of the crystallization of sodium carbonate.

Sulfates of sodium and potassium are common constituents of evaporates deposited on, or immediately beneath, the surface in arid regions. They contain sodium chloride and sodium carbonate as frequent constituents.

RUBIDIUM AND CESIUM IN IGNEOUS ROCKS

The heavy alkali metals, rubidium and cesium, occur together almost constantly in Nature. As a general rule they follow potassium, as far as their manner of occurrence is considered. Unlike lithium, they become incorporated in salic minerals during crystallization. They resemble potassium chemically, but their ionic dimensions are even greater than that of potassium. This fact is responsible for their extremely pronounced concentration in the late crystallates, particularly in those of granitic composition, whereas in nepheline syenites the degree of their concentration is considerably smaller. The ionic radii of the alkali metals increase systematically from lithium (radius 0.78 kX) to rubidium (radius 1.49 kX) and cesium (radius 1.65 kX), and therefore cesium is most pronouncedly enriched in the late crystallates.

Table 12.6 shows the content of rubidium and cesium in the various classes of igneous rocks. These metals are particularly enriched in greisen, in which they are evidently largely present in lepidolite. They are thus rather mobile in pneumatolytic processes.

According to Sahama (1945*b*), cesium is absent in the rocks of the Basement Complex of southern Lapland. In general, the pre-Cambrian rocks of Finland are poorer in cesium than are the mainly Caledonian and Variscan rocks analyzed by Goldschmidt, Berman, Hauptmann, and Peters (1933) and by Goldschmidt, Bauer, and Witte (1934).

Cesium and, in particular, rubidium are typical representatives of the dispersed elements of Vernadsky (1924). According to him, such elements very seldom, if ever, form independent minerals. Notwithstanding the fact that rubidium is one of the most abundant trace elements and, moreover, considerably more abundant than cesium, no independent rubidium minerals have ever been found to exist. This is caused by the fact that the radius of Rb^+ (1.49 kX) is quite similar to that of K^+ , (1.33 kX), and therefore rubidium is concealed in the minerals of the much more abundant potassium. Cesium, on

the other hand, owing to its considerably greater ionic size (radius 1.65 kX), tends to accumulate in the last residual liquors, with the result that sometimes its concentration grows high enough to give rise to the formation of pollucite, $\text{Cs}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}_{<1}$. Pollucite contains 36.5 per cent Cs_2O and up to 3.73 per cent Rb_2O and is a comparatively rare mineral. If the concentration of cesium does not increase enough to result in the formation of pollucite, the difference

TABLE 12.6
CONTENT OF RUBIDIUM AND CESIUM IN IGNEOUS ROCKS

Rock	Rb	Cs
	(g/ton)	
Gabbros, Germany, composite (Goldschmidt, Berman, Hauptmann, and Peters, 1933).....	18	not detected
Granites, Germany, composite (Goldschmidt, Bauer, and Witte, 1934).....	830	40
Greisen rocks, Erzgebirge, Germany, composite (Goldschmidt, Bauer, and Witte, 1934).....	1,830	67
Nepheline syenites, composite (Goldschmidt, Bauer, and Witte, 1934).....	440	6
Phonolites, composite (Goldschmidt, Bauer, and Witte, 1934).....	330	not detected
Pre-Cambrian granites of Finland (Erämetsä, Sahama, and Kanula, 1941).....	1,180-1,270	0-47
Basement Complex of southern Lapland (Sahama, 1945b):		
Ultrabasics.....	0	0
Gabbros and dolerites.....	0	0
(individual samples up to).....	(27)	
Granites.....	455-910	0
Syenites.....	550	0

in the ionic dimensions of rubidium and cesium is large enough to cause a separation of these metals in the late crystallates. The result is the enrichment of cesium in pegmatites in relation to rubidium.

Schiebold (1931) has shown that theoretically both rubidium and cesium are able to form feldspar structures. Rubidium, as a matter of fact, is nearly always present in potash feldspars. The green amazonites, according to Goldschmidt, Bauer, and Witte (1934), are particularly rich in rubidium. The potash feldspars of pegmatites are often considerably enriched in both rubidium and cesium, whereas the sodium minerals are devoid of these metals, especially cesium. Among the potash feldspars so far investigated, the highest rubidium and cesium content reported occurs in a microcline perthite from the

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Varuträsk pegmatite in northern Sweden, which contains 3.3 per cent Rb_2O and 0.6 per cent Cs_2O (Quensel, 1937). Although both rubidium and cesium in pegmatites are heavily enriched in regard to potassium, there is evidence indicating that, in addition, the Cs:Rb ratio in pegmatites differs somewhat from that found in the rocks formed during the main stage of crystallization. In pegmatites, cesium is even more abundant in relation to potassium than rubidium is. Compared with the content of rubidium in granites and nepheline syenites and in their potash feldspars, the content in granite pegmatites is considerably higher. The rule is valid also in case of cesium. In leucite the content of rubidium and cesium is very much higher than in the rock-making potash feldspars. Goldschmidt, Bauer, and Witte (1934) report up to 0.034 per cent Rb_2O and 0.023 per cent Cs_2O in leucite.

As shown by Adamson (1942), the Cs:Rb ratio in the microcline perthite from Varuträsk is higher than in any igneous rock or pegmatite so far investigated. At Varuträsk the high concentration of cesium has caused abundant formation of pollucite, which is quarried as a cesium ore.

Along with the feldspars, the micas also are important carriers of rubidium and cesium in igneous rocks, particularly in pegmatites. The high content of these metals in lepidolite is well established. Lepidolite contains up to 1.73 per cent Rb_2O and 0.72 per cent Cs_2O . As much as 1.49 per cent Rb_2O is reported in zinnwaldite. Goldschmidt, Bauer, and Witte (1934) found 0.40 per cent Rb_2O and 0.015 per cent Cs_2O in a muscovite from a granite pegmatite and 0.39 per cent Rb_2O and 0.048 per cent Cs_2O in lepidomelane from nepheline syenite pegmatite. Biotite is reported to contain in excess of 3 per cent Cs_2O . Erämetsä, Sahama, and Kanula (1941) found up to 1 per cent Rb_2O in phlogopite from contact metamorphic limestones.

The distribution of rubidium and cesium between feldspars and micas is illustrated in the accompanying tabulation by the analyses made by Erämetsä, Sahama, and Kanula (1941).

These analyses show that the rubidium and cesium content is higher in the micas than in the feldspars.

Stevens and Schaller (1942) report the average content of lithium, rubidium, and cesium in micas from pegmatites given in Table 12.7. They have established an increase in the content of the rare alkalies, in both their individual and their total content, with the successive stages of hydrothermal replacement in pegmatites of southern Cali-

fornia. The replacement starts with a sodium phase, consisting chiefly of albitization and the formation of muscovite, and ends with a lithium phase, which culminates in the production of large amounts of lepidolite and lithium tourmaline.

MINERALS ANALYZED	Rb ₂ O	Cs ₂ O
	Per Cent	
<i>Pegmatitic granite, Luikonlahti, Finland:</i>		
Biotite	0.35	0.003
Microcline	0.17	0
<i>Pegmatite, Skogsbole, Kemio, Finland:</i>		
Muscovite	~2.5	0.02
Albite (cleavelandite) .	0.08	0.001

Ahrens (1947a) states that, together with amazonite, pollucite is probably the second richest rubidium mineral; lepidolite is the richest.

Rubidium and cesium are also enriched in many beryl varieties found in pegmatites and in miarolitic cavities in granites, but the cause of their concentration in this mineral is still unknown.

TABLE 12.7
AVERAGE CONTENT OF LITHIUM, RUBIDIUM, AND CESIUM IN MICAS

Compound	Paragonite	Muscovite	Biotite	Lepidolite
Li ₂ O	0.31	0.26	0.71	4.90
Rb ₂ O	0.08	0.14	0.59	1.35
Cs ₂ O	0	0.06	0.30	0.24
Total	0.39	0.46	1.60	6.49

They are also present in the rare pegmatite mineral rhodizite, $\text{KNaLi}_4\text{Al}_4[\text{Be}_3\text{B}_{10}\text{O}_{27}]$.

Also in minerals of late hydrothermal veins rubidium and cesium accompany potassium, e.g., in adularia. Many mineral waters contain rubidium and cesium, apparently derived from thermal waters. The greater volatility of cesium compounds, as compared with the corresponding rubidium and potassium compounds, causes the enrichment of cesium in the sublimates of potash-rich volcanic rocks. The lavas of Vesuvius contain, as a sublimate, the borofluoride avo-

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gadrite, $K[BF_4]$, in which potassium is replaced by significant quantities of cesium.

CYCLE OF RUBIDIUM AND CESIUM

Like the other alkali metals, rubidium and cesium are also brought into solution during weathering. As pointed out previously in this chapter, potassium is subsequently almost quantitatively removed from the solution and precipitated, by adsorption, in clays. This fact is due to its small ionic potential. That of rubidium and cesium is still smaller, and therefore these metals follow potassium during the minor cycle and become adsorbed in argillaceous sediments still more completely than potassium does. As pointed out by Noll (1931),

TABLE 12.8
CONTENT AND ABUNDANCE RATIOS OF POTASSIUM, RUBIDIUM,
AND CESIUM IN SOME GEOCHEMICAL MATERIALS

MATERIAL	K	Rb	Cs	Rb:K	Cs:K
	g/ton				
Igneous rocks	25,900	310	7	0 012	0 00027
Argillaceous sediments	27,000	300	12	0 011	0 00044
Sea water	380	0 2	~0 002	0 00053	0 0000053

cesium is adsorbed more quantitatively than rubidium is. The Rb:K and Cs:K ratios of hydrolyzate sediments tend to be greater than the corresponding ratios in igneous rocks (see Table 12.8). From the pronounced adsorption of rubidium and cesium it follows that only a very small part of these metals remains in sea water and is finally incorporated in the evaporates. The studies of Goldschmidt and his co-workers (Goldschmidt, Berman, Hauptmann, and Peters, 1933; Goldschmidt, Bauer, and Witte, 1934) have revealed that the Rb:K ratio in evaporates (carnallite) is of the same order as that in sea water, but both the Rb:K and the Cs:K ratios are lower than in igneous rocks. The abundance of the three alkali metals and their abundance ratios in some geochemical materials of importance in the minor cycle are presented in Table 12.8 on the basis of Tables 2.3, 5.52, and 6.17. The values show that the content of rubidium and cesium in sea water is strongly reduced with respect to that of potassium. It is evident that the same rule is also valid in the evaporate sediments.

THE ALKALI METALS

The content of rubidium and cesium in sediments and their derivatives is shown by the values recorded in Table 12.9. The number of analyses available is still deplorably small.

In spite of the scarcity of rubidium and cesium in evaporates, the potassium salts are the most important industrial sources of these metals. They are recovered as by-products of salt-mining and purification processes. The readily soluble potassium salts are technically a more valuable source of rubidium and cesium than are the silicate minerals of pegmatites. However, some pegmatites exceptionally rich in rubidium and cesium minerals are mined as ores of these metals.

TABLE 12.9

CONTENT OF RUBIDIUM AND CESIUM IN SEDIMENTS AND THEIR DERIVATIVES

MATERIAL	Rb	Cs
	g/ton	
Shales, composite (Goldschmidt, Bauer, and Witte, 1934)	300	12
Red clay (Goldschmidt, Bauer, and Witte, 1934)	391	13
Glauconite (Goldschmidt, Bauer, and Witte, 1934)	555	15
Laterite-bauxite ores (Landergrén, 1948)	5	
Bog iron ores, Finland (Landergrén, 1948)	8	
Marine oolitic-siliceous iron ores (Landergrén, 1948)	7	
Marine siderite ores (Landergrén, 1948)	5	
Quartzites, southern Lapland (Sahama, 1945 <i>b</i>)	273	
Aluminum-rich schists, southern Lapland (Sahama, 1945 <i>b</i>)	540-730	
Carbonate rocks, southern Lapland (Sahama, 1945 <i>b</i>)	0	

THE ALKALI METALS IN THE BIOSPHERE

Lithium is reported to be present in many plants and animals as a variable microconstituent. According to Strock (1936), it may become enriched in plant and coal ashes. Tobacco ashes contain up to 0.44 per cent Li. Lithium is evidently also concentrated in soil; Mitchell (1944) reports a content varying from 30 to 5,000 g/ton Li therein. Lithium is more toxic than sodium and potassium and so far has not been shown to possess any biological role.

Sodium and potassium are definitely biophile elements.

Sodium is probably a universal microconstituent of plants, and some species are known which accumulate it. Marine plants are the richest in sodium. The content of this metal in animals is still higher than in plants. Sodium is the chief circulating cation in the extracellular liquids in animals, and its content therein is always higher than in the cells. Sodium is of great importance in biological systems

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as a transport element, and it is essential in tissues of higher plants and animals. Further, it helps to maintain the ionic balance of body fluids. However, it is claimed that some plants and insects contain practically no sodium or are able to lose most of their supply of this metal without disturbance in their physiological functions.

Potassium is an essential constituent of all plants, in which its content is higher than that of sodium. Potassium is also a universal constituent of all animals, in which it is found chiefly in the cells, in analogy to its manner of occurrence in plants, whereas sodium circulates in the extra-cellular fluids and thus maintains its manner of occurrence in sea water. The higher land animals usually contain somewhat more potassium than sodium. The bulk of potassium in plants occurs as K^+ ions, and this is the case also with the higher animals, in which potassium occurs mostly as phosphate, but organic compounds carrying potassium, e.g., lipides, are known, in addition. Potassium is a factor in the growth of plants and animals: in the plant it is essential for the synthesis and function of chlorophyll; in the animals it is the chief cation within the cells.

Rubidium is frequently found in plants, and some species are able to concentrate it. The ashes of sugar cane contain as much as 0.2 per cent Rb. Cesium is also present therein. Mitchell (1944) found a content of 100–2,000 g/ton Rb in soil. In higher animals rubidium is frequently present as a microconstituent, but in lower animals and plants its occurrence is sporadic. Rubidium may perhaps replace potassium in some plants. It is toxic to higher animals.

Cesium often accompanies rubidium in the biosphere. Mitchell (1944) reports up to 500 g/ton Cs in soil. In the absence of potassium, cesium is toxic to most plants, and it is also toxic to animals. It is a doubtful microconstituent of some animals.

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE cosmic abundance of beryllium and that of its neighbors in the Periodic System, lithium and boron, is remarkably low. So far, the abundance of beryllium in igneous rocks and in meteorites is not known in all details. A summary of its abundance values is given in Table 13.1. The beryllium content of the sulfide and metal phases of the meteorites is very low. Beryllium is present in the atmospheres of the Sun and of other stars (see chap. 2).

TABLE 13.1
ABUNDANCE OF BERYLLIUM

Material	Be (g/ton)
Meteoritic iron.....	unknown
Troilite.....	unknown
Silicate meteorites (Goldschmidt, 1937b).....	1
Igneous rocks (Goldschmidt and Peters, 1932a).....	2
Igneous rocks (Goldschmidt, 1937b).....	6
Igneous rocks (Sandell and Goldich, 1943).....	<7

Notwithstanding the difference in the valence of beryllium and aluminum, these metals resemble each other chemically. Like aluminum, beryllium is also geochemically strongly lithophile.

BERYLLIUM IN IGNEOUS ROCKS

In the lithosphere, beryllium is appreciably enriched in the uppermost crust. It is a typically oxyphile element. No detailed determinations are available to show the average content of beryllium in the various groups of igneous rocks. The values recorded in Table 13.2 establish the presence of regional variations in the beryllium content of the upper lithosphere. The values also illustrate the pronounced tendency of beryllium to become enriched toward the late stages of magmatic differentiation. Thus both granites and nepheline syenites are high in beryllium, but in the alkalic rocks low in silica the degree of enrichment is considerably higher than in the silica-rich granites.

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Sahama and Vähätalo (1939*a*) have also established the concentration of beryllium in the residual solutions of diabase magmas.

The study of the crystal structures of beryllium minerals leads to the conclusion that the co-ordination number of the bivalent beryllium ion in regard to oxygen is always 4. This fact is evidently due to the small size of the Be^{2+} ion (radius 0.34 kX), which lies not far from the Si^{4+} ion (radius 0.39 kX) in this respect. Owing to this similarity, it would be natural to assume that beryllium would preferably replace silicon in the $[\text{SiO}_4]$ tetrahedra. As a matter of fact, this substitution seems to be the most important manner of occurrence of beryl-

TABLE 13.2
CONTENT OF BERYLLIUM IN IGNEOUS ROCKS

Rock	Be (g/ton)
Olivinites and plagioclase rocks (Goldschmidt and Peters, 1932 <i>a</i>).....	0
Gabbros and diabases (Goldschmidt and Peters, 1932 <i>a</i>).....	<3.6
Granites (Goldschmidt and Peters, 1932 <i>a</i>).....	3.6
Nepheline syenites (Goldschmidt and Peters, 1932 <i>a</i>).....	36
Dark nepheline-bearing rocks (Goldschmidt, Hauptmann, and Peters, 1933).....	up to 360
Acidic igneous rocks, average (Sandell and Goldich, 1943).....	7
Ultrabasic rocks of southern Lapland (Sahama, 1945 <i>b</i>).....	0
Gabbros and dolerites of southern Lapland (Sahama, 1945 <i>b</i>).....	0
Granites of southern Lapland (Sahama, 1945 <i>b</i>).....	1
Syenites of southern Lapland (Sahama, 1945 <i>b</i>).....	2

lium in mineral structures. The rocks usually contain too little beryllium to allow the formation of its independent minerals, and therefore it is contained in the structures of other minerals. Silicic igneous rocks and particularly nepheline syenites may carry notable amounts of beryllium in their alkali feldspars, nepheline, sodalite, micas, tourmaline, alkali amphiboles, and alkali pyroxenes. Goldschmidt and Peters (1932*a*) found up to 36 g/ton Be in muscovite, somewhat more in biotite, and 360 g/ton in aegirite. Filippov and Tolmačev (1935) report a maximum of 150 g/ton Be in amazonite. The minerals listed above undoubtedly carry the bulk of the beryllium present in the upper lithosphere. In these minerals the Be^{2+} ions do not occur outside the silicon-oxygen framework but actually replace silicon within the $[\text{SiO}_4]$ tetrahedra. It must also be borne in mind that, according to Schiebold (1931), beryllium cannot replace calcium in the anorthite structure and that therefore there exists no "beryllium anorthite."

The enrichment of beryllium in granite and nepheline syenite pegmatites is a fact long known to mineralogists. As pointed out by Goldschmidt and Peters (1932*a*), the enrichment is evidently due to the small size of the beryllium ions, which consequently are not capable of hiding in the structures of common rock-making minerals but become, instead, enriched in the residual solutions. According to Wickman (1943; see chap. 5), another cause is the low charge of the beryllium ion, which gives a weaker bond than, for instance, in the case of silicon. Therefore, beryllium becomes enriched in pegmatites, which often contain independent beryllium minerals, the more important among which are the following:

Chrysoberyl,	Al_2BeO_4
Beryl,	$\text{Al}_2\text{Be}_3[\text{Si}_6\text{O}_{18}]$
Phenakite,	$\text{Be}_2[\text{SiO}_4]$
Euclase,	$\text{Al}[\text{BeSiO}_4\text{OH}]$
Eudidymite and epididymite,	$\text{Na}[\text{BeSi}_3\text{O}_7\text{OH}]$
Meliphanite,	$(\text{Ca}, \text{Na})_2[(\text{Be}, \text{Al})\text{Si}_2\text{O}_6\text{F}]$
Leucophane,	$(\text{Ca}, \text{NaH})_2[\text{BeSi}_2\text{O}_6(\text{OH}, \text{F})] (?)$
Gadolinite,	$\text{Y}_2\text{Fe}[\text{O} \text{BeSiO}_4]$
Helvite, danalite, genthelvite,	$(\text{Mn}, \text{Fe}, \text{Zn})_3[\text{S}_2 (\text{BeSiO}_4)_6]$

Chrysoberyl may be structurally derived from olivine by replacing Si by Be and 2Mg by 2Al. In beryl and phenacite, beryllium does not replace silicon, but, in the other berylliosilicates listed above, the complex anion framework constitutes a Be-Si-O network. The ratio Be:Si varies, being 1:1 in euclase, helvite, and gadolinite; 1:2 in melinophane and leucophane; and 1:3 in eudidymite and epididymite. In the minerals of plumasitic pegmatites, which contain alumina in excess over potash and soda, the Be-Si-O network is linked to aluminum, e.g., in euclase and beryl. In agpaitic pegmatites, on the other hand, in which potash and soda predominate over the amount of alumina, chiefly Na^+ and Ca^{2+} occupy the positions of cations outside the network, e.g., in eudidymite, epididymite, meliphanite, and leucophane. These minerals are found mainly in nepheline syenite pegmatites.

Other independent beryllium minerals are the rare oxide bromelite, BeO , some phosphates, and borates. Beryllonite, $\text{NaBe}[\text{PO}_4]$, and herderite, $\text{CaBe}[(\text{OH}, \text{F})|\text{PO}_4]$, are pegmatite minerals. Hambergite, $\text{Be}_2[\text{OOH}|\text{BO}_2]$, is found in agpaitic pegmatites.

Beryl, with a content of 11.5–13.5 per cent BeO , is the technically most important mineral of beryllium. Industrially significant beryllium deposits occur, as a rule, only in granite pegmatites, whereas the nepheline syenites have no economic importance in this respect. The

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explanation is that, notwithstanding the usually higher content of beryllium in nepheline syenites as compared with granites, the degree of its enrichment during the last stages of formation of alkalic rocks is considerably lower than during the crystallization of granitic residual liquors. The main constituents of nepheline syenites usually carry more beryllium than do the granite minerals, and therefore the bulk of this metal is removed from the alkalic melts during the main stage of their crystallization.

Beryllium is not enriched in products of normal contact metamorphism of shales. However, noteworthy concentrations of beryllium are often present in the skarn zones formed by pneumatolytic and metasomatic processes at igneous contacts in limestones. Helvite is a common constituent of skarn rocks. Among other skarn minerals, grossularite, epidote, allanite, and particularly idocrase (vesuvianite) are beryllium-bearing. Idocrase may contain in excess of 1 per cent BeO. A content of 0.1 per cent BeO has been established in axinite, and allanite (orthite) may sometimes be rich in beryllium (beryllian allanite with nearly 4 per cent BeO). Beryllium is also present in hydrothermal solutions and may become incorporated in zeolites and other late hydrothermal minerals.

Landergren (1948) found up to 100 g/ton Be in the skarn iron ores of central Sweden. He concludes that, in general, there seems to occur an enrichment of beryllium in connection with the enrichment of iron. Beryllium is not enriched in minerals and rocks genetically connected with pneumatolytic deposition of cassiterite. The only exception is zinnwaldite, which may contain nearly 360 g/ton Be (Goldschmidt and Peters, 1932a).

CYCLE OF BERYLLIUM

During the processes of weathering and formation of sediments, beryllium closely follows the course of aluminum, being enriched, along with this metal, in clays, bauxites, recent deep-sea deposits, and other hydrolyzate sediments. This is due to the similarity of the basic properties and solubilities of the hydroxides of these metals. Even though the radii and the charges of the Be^{2+} and Al^{3+} ions differ from each other, their ionic potentials are rather similar ($\Phi_{\text{Be}^{2+}} = 5.9$; $\Phi_{\text{Al}^{3+}} = 5.3$), and therefore the two metals follow each other into the hydrolyzates during the hydrolytic decomposition of their salts. Wickman (1944) confirmed the fact that beryllium is an element of the hydrolyzates.

The content of beryllium in sediments and sedimentary rocks is presented in Table 13.3, which contains, in addition, information on the beryllium content of some metamorphic rocks. As in the case of aluminum, the content of beryllium does not materially decrease during contact and regional metamorphism.

Szelényi (1937) found no material difference in the beryllium content of clays and bauxites, whereas some kaolins were low in this

TABLE 13.3
CONTENT OF BERYLLIUM IN SEDIMENTS, SEDIMENTARY ROCKS,
AND SOME METAMORPHIC ROCKS

Material	Be (g/ton)
Kaolin (Szelényi, 1937)	up to 180
Bauxite (Szelényi, 1937)	1.8-36
Lateritic and bauxitic iron ores (Landergren, 1948) .	5
Clay (Szelényi, 1937)	up to 36
Clay, Chilean nitrate deposits (Goldschmidt and Peters, 1932a)	~3.6
Bottom sediment, Tyrrhenian Sea (Landergren, 1948)	13
Deep-sea oozes (Goldschmidt and Peters, 1932a) . .	0
Red clay (Goldschmidt and Peters, 1932a)	<3.6
Manganese nodule (Goldschmidt and Peters, 1932a)	0
Shales (Goldschmidt and Peters, 1932a)	3.6
Bog ores (Landergren, 1948)	7
Sedimentary iron ores (Goldschmidt and Peters, 1932a)	<3.6
Marine iron ores (Landergren, 1948)	10
Sedimentary manganese ores (Goldschmidt and Peters, 1932a)	<3.6
Quartzites of southern Lapland (Sahama, 1945b) . .	0
Leptitic and aluminum-rich schists, southern Lap- land (Sahama, 1945b)	1
Black (carbonaceous) schists, southern Lapland (Sahama, 1945b)	<1
Carbonate rocks, southern Lapland (Sahama, 1945b)	0

metal. Taken as a whole, the content of beryllium in sediments and sedimentary rocks is still rather incompletely known.

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Beryllium is concentrated by some plants, especially by those growing in berylliferous areas. The ashes of wheat are reported to contain as much as 2 per cent Be. Goldschmidt and Peters (1933c) found beryllium enriched in coal ashes. However, the biological role of this metal is still unknown, and the toxicity of beryllium salts is claimed to be due to the acid radical or to their hydrolytic decomposition. It is possible that beryllium only accompanies aluminum in organisms. As stated by Fearon (1933), it may often have been mistaken for aluminum in biological analyses.

MAGNESIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

MAGNESIUM is the scarcest of the eight main elements of the upper lithosphere. According to Clarke and Washington (1924), the average magnesium content of igneous rocks is 2.09 per cent, whereas the content of potassium, which precedes magnesium, is 2.59 per cent. The average content of magnesium in silicate meteorites is 16.00 per cent (Merrill, 1916; recalculated by Goldschmidt, 1937*b*). No magnesium is present in the metal and sulfide phases of the meteorites. Magnesium is also one of the most abundant constituents of the solar atmosphere. In the sunspots its abundance is still higher.

In the silicate meteorites the abundance of magnesium, calculated as atoms per 100 atoms of silicon, is ten times as high as its corresponding abundance value in igneous rocks. The explanation is that the ferromagnesian ortho- and metasilicates—olivine and the Ca- and Al-free pyroxenes—predominate in the silicate meteorites, whereas the femic magnesium minerals of igneous rocks, on an average, are much less abundant than the feldspars, quartz, and some other minerals.

Magnesium is strongly lithophile, and in the Earth it is almost quantitatively contained in the silicate shell. In the upper lithosphere magnesium is combined exclusively with oxygen. The magnesium sulfide, MgS , is not known as a mineral, which affords proof of the strongly oxyphile character of magnesium.

With reference to its terrestrial occurrence, magnesium, in addition, belongs to the group of the biophile elements.

MAGNESIUM MINERALS

Unlike the alkali metals, magnesium is able to build both simple and complex inorganic compounds which are stable under the conditions met in Nature. The most important silicate minerals of magnesium are the following:

Olivine group
 Forsterite
 Garnet group
 Pyrope
 Cordierite
 Pyroxene group
 Diopside
 Pigeonite
 Augite
 Enstatite
 Amphibole group
 Cummingtonite
 Actinolite series
 Hornblende
 Anthophyllite
 Chrysotile
 Sepiolite
 Talc
 Mica group
 Phlogopite
 Biotite
 Chlorite group
 Magnesian clay minerals

With reference to the crystal structure of these minerals, it is important to note that none belongs to the structural group of the tectosilicates. It was mentioned in chapter 5 that this is due to the occurrence of the Mg^{2+} ion in 6-co-ordination, the result being that the three-dimensional tectosilicate framework of linked $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra cannot neutralize the magnesium ions electrically. Because the light constituents of both igneous and metamorphic rocks, especially the feldspars and the feldspathoids, belong structurally to tectosilicates, magnesium is almost totally confined to the early-crystallizing dark constituents of rocks. On the other hand, calcium with a co-ordination number from 6 to 9 begins to crystallize later and preferentially forms plagioclase feldspars.

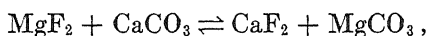
The following are the most important among the nonsilicate minerals of magnesium, the salt minerals not being considered:

Dolomite,	$\text{CaMg}[\text{CO}_3]_2$
Magnesite,	MgCO_3
Spinel,	MgAl_2O_4
Geikielite,	MgTiO_3
Periclase,	MgO
Brucite,	$\text{Mg}(\text{OH})_2$
Sellaite,	MgF_2

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The magnesium carbonates, dolomite and magnesite, are of considerable petrological and geochemical importance. The oxide minerals of magnesium, with the exception of spinel, are rare. The salt minerals of magnesium (see under "Cycle of Magnesium," p. 453) are common constituents of many evaporate sediments.

Contrary to fluorite, which is a common constituent of late magmatic crystallates, sellaite is not stable in igneous rocks. It is rare and its most important manner of occurrence is in dolomitic limestones along with anhydrite. Its stability relationships were investigated thermochemically by Sahama (1945*a*), who found that the assemblage sellaite-calcite, represented by the equation



is stable at high temperatures, whereas at low temperatures the assemblage fluorite-magnesite is stable. Both fluorite and sellaite are stable in dolomite at low temperatures. If magnesite is present, sellaite will be formed at higher temperatures at the expense of fluorite, according to the above equation.

Sahama (1945*a*) has also called attention to some other differences in the abundance of calcium and magnesium minerals. Phosphorus is always combined with calcium and forms apatite. The corresponding magnesium mineral, wagnerite, $\text{Mg}_2[\text{F}|\text{PO}_4]$, is rare. On the other hand, periclase, MgO , and brucite, $\text{Mg}(\text{OH})_2$, are more common minerals than lime, CaO , and portlandite, $\text{Ca}(\text{OH})_2$.

The co-ordination number of magnesium in the structures of most of its minerals is 6. In some structures, for example, in garnet and in spinel, its co-ordination number is 4.

MAGNESIUM IN IGNEOUS ROCKS

Basic and, particularly, ultrabasic rocks form the proper surroundings of magnesium in the upper lithosphere. The average compositions calculated by Daly (1933) for the various rocks of the calc-alkalic differentiation series (see Table 5.32) show that magnesium is very strongly enriched in the silicate minerals which separated from the magma during the early stages of crystallization. Therefore, dunites and similar rocks are high in magnesium. The first products of magmatic differentiation, which are usually formed prior to the separation of the early magmatic sulfides, and the silicate minerals accompanying the early-separated titaniferous iron ores contain magnesium, along with ferrous iron, in the form of the orthosilicate

olivine. The early olivines are rich in the magnesian component, forsterite. In addition, the corresponding metasilicate, enstatite, occurs often as a constituent of the early crystallates. During the main stage of crystallization magnesium—again together with ferrous iron—is the most important cation to become incorporated in femic minerals.

The manner of occurrence of magnesium in igneous rocks is consequently characterized by the diadochy Mg^{2+} - Fe^{2+} , the natural explanation of which is the equal size of the two ions ($r_{\text{Mg}^{2+}} = 0.78 \text{ kX}$; $r_{\text{Fe}^{2+}} = 0.83 \text{ kX}$). The diadochy is complete in nearly all mineral groups of petrological importance. Cordierite seems to form the only exception to this rule, but this mineral is but rarely found as a constituent of primary igneous rocks. The cordierites are usually rather poor in iron, but some rare types have been encountered which are iron-rich. The iron-rich members of certain amphibole series not met as constituents of igneous rocks, e.g., the actinolite series, are similarly unknown. The general rule has it that magnesium, compared with iron, becomes enriched in rock-making minerals when their crystallization temperatures are relatively high. The melting temperatures of the silicate minerals of magnesium, as a matter of fact, lie rather high and are well in excess of those of the corresponding ferrous minerals. It is evident that the Mg^{2+} ion is very strongly bound within the structures, that is, its energy of migration is high. As was pointed out in chapter 5, this is due to the fact that the radius of the Mg^{2+} ion is not very far from the optimum value required by the 6-co-ordination. The Mg^{2+} ion has just the proper size to fill out completely the space between six oxygen ions in contact with one another, without pushing them apart. Consequently, a strong bond is generated between magnesium and the oxygen ions. In the case of Fe^{2+} , which is greater than Mg^{2+} , the bond is weakened, with a resulting decrease in the melting temperature of the silicates in question. Thus ferrous iron becomes concentrated in the mother-liquor.

The regular change of the Fe:Mg ratio during the differentiation was discussed in chapter 5. With reference to the manner of distribution of the two metals among the femic constituents of igneous rocks, it must be noticed that in the pyroxenes and amphiboles of the calc-alkalic igneous rocks magnesium nearly always predominates if a sufficient supply of it has been available. On the other hand, the alkalic rocks are, on an average, considerably lower in magnesium, and therefore ferrous iron predominates over magnesium in their py-

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roxenes (aegirite-aegirinaugite series) and amphiboles (riebeckite series).

The common rock-making oxides in igneous rocks are entirely different from the silicate minerals; they are chiefly iron compounds with only a very low content of magnesium. The magnesium compound corresponding to ilmenite, viz., geikielite, MgTiO_3 , is only a mineralogical curiosity; and magnetite, the most abundant among the opaque accessory constituents of igneous rocks, is almost totally free of magnesium. The only common oxide mineral of magnesium, viz., spinel, MgAl_2O_4 , is actually irrelevant to rocks belonging to the main stage of crystallization.

The scarcity of geikielite is explained by Sahama and Torgeson (1949) on thermochemical reasons. The mixture geikielite + olivine is stable at high temperatures, whereas the mixture ilmenite + olivine is stable at low temperatures.

Forsterite and enstatite, the early-crystallized constituents of ultrabasics, often succumb to autometamorphism and react with aqueous solutions, whereby serpentine and talc and often also chlorite, orthorhombic amphiboles, actinolite, and still other minerals are formed.

BIOGEOCHEMISTRY OF MAGNESIUM

Magnesium is a constant microconstituent of lower plants. In the higher plants it is, as a porphyrin derivative, an essential constituent of chlorophyll. The foremost biochemical importance of magnesium lies in its role as the catalytic metal in photosynthetic processes based on the existence of chlorophyll. Seeds contain magnesium, along with calcium, as inositol hexaphosphate. Magnesium is also important as the activator of some enzymes and in the phosphate transport in animals. Therefore, it is a factor in their growth.

Some marine organisms are very rich in magnesium. Up to 25 per cent MgCO_3 may be incorporated in the calcareous parts of some marine algae. Lower contents are reported in the shells and skeletons of other marine organisms (foraminifers and echinoderms). In certain organisms the proportion of MgCO_3 seems to be a function of temperature: according to Clarke and Wheeler (1922), organisms living in warm water are regularly higher in magnesia than those dwelling in cold water.

In higher animals magnesium is constantly found in the skeletal parts, muscles, and nerve tissue. In the skeleton, magnesium and cal-

cium are closely associated, and magnesium accompanies, supplements, or replaces calcium therein.

Magnesium, like calcium, becomes enriched in certain bioliths.

CYCLE OF MAGNESIUM

The behavior of magnesium during the processes of weathering and the formation of sediments is illustrated by the summary of magnesium contents given in the accompanying tabulation, based on Tables 2.3, 5.52, and 6.7.

Material	MgO (Per Cent)
Igneous rocks	2.09
Salts of lake and river waters	3.41
Salts of sea water	3.69
Argillaceous sediments	1.48

The magnesium content of argillaceous sediments is not very much lower than that of igneous rocks. During chemical weathering, magnesium is released mainly as the soluble chloride, MgCl_2 , and sulfate, MgSO_4 . Another portion of magnesium is transported, partly as chemically undecomposed, finely ground mineral particles and partly as magnesium-bearing clay minerals, which are derived particularly from basic and ultrabasic rocks during the weathering (chap. 5). This portion is finally deposited in the hydrolyzates. Still another part of magnesium becomes incorporated in the clay minerals as a result of base-exchange reactions.

The cycle of magnesium differs rather pronouncedly from that of calcium. According to the discussion presented in chapter 6, calcium exceeds all other cations in solution in river waters, but in the sea by far its greatest part is removed from solution by precipitation as carbonate, caused either by marine organisms or by inorganic processes. The result is a low content of dissolved calcium in sea water. Magnesium, on the other hand, is nearly as abundant in river water as in the sea. Many of its salts are readily soluble, and therefore its bulk remains in sea water, occupying the next place in abundance in the ocean, right after chlorine and sodium. However, the enrichment of magnesium in sea water is not quite so pronounced as that of sodium (see Table 6.19), and its content remains relatively stable because of the additional quantities transported to the sea by rivers. Like sodium, magnesium remains largely in the sea, although it is partly precipitated as carbonate. In its behavior during the exogenic cycle magnesium therefore occupies a position intermediate between

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sodium and calcium, following, however, a course closer to the first-mentioned metal.

A small part of magnesium becomes incorporated in the evaporates, along with calcium and the alkali metals, particularly sodium. Because its salts are readily soluble, magnesium is usually present only among the compounds crystallized during the last stages of the evaporation of the brines, and various magnesium and potassium-magnesium salts are then formed. Some of the salts were mentioned in chapter 12. The alkali-free magnesium salts found in the evaporates include the chloride bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and the sulfates kieserite, $\text{Mg}[\text{SO}_4] \cdot \text{H}_2\text{O}$; hexahydrate, $\text{Mg}[\text{SO}_4] \cdot 6\text{H}_2\text{O}$; and epsomite, $\text{Mg}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$. The presence of magnesium salts affords proof of the marine origin of the deposits and excludes the possibility of their lacustrine crystallization. This rule refers to the sulfates and chlorides of magnesium. On the other hand, magnesium is an important constituent of evaporate sediments consisting of borates (see chap. 16).

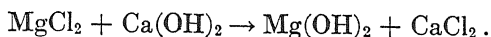
A number of magnesium phosphates of secondary origin are known as minerals, e.g., struvite, $(\text{NH}_4)\text{Mg}[\text{PO}_4] \cdot 6\text{H}_2\text{O}$, and bobierite, $\text{Mg}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$, which are found in guano. Hörnesite, $\text{Mg}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$, is the arsenate corresponding to bobierite in composition.

The precipitation of magnesium hydroxide starts at a pH of 10. It might thus be possible that brucite is formed in alkali soil. In sea water, even during active photosynthesis, the pH evidently does not attain a value high enough for the precipitation of magnesium as hydroxide.

Eskola (1914) has shown that magnesium may be rather mobile in metasomatic processes. Thus, for example, some magnesium-rich rocks of southwestern Finland are explained as a result of a magnesia metasomatism of acidic leptites, whereby very considerable amounts of magnesia were added which replaced the alkalies and lime in the original rocks. Cordierite and anthophyllite are typical minerals in the metasomatic rocks rich in magnesia, and sulfide-ore deposits are often genetically connected with the metasomatic rocks.

The potassium-magnesium salts of the evaporate sediments, particularly carnallite, are important ores of magnesium. Therefore, the production of magnesium from salt minerals is closely connected with that of potassium. Magnesium is also obtained from dolomite, mag-

nesite, and brucite. Sea water is an important source of magnesium, which is removed therefrom as the hydroxide:



MAGNESIUM CARBONATE

Along with pure calcium carbonate, the precipitates also contain dolomite, which is the double carbonate of calcium and magnesium. Small amounts of authigenic dolomite are common in deep-sea deposits. Magnesium carbonate is more soluble than calcium carbonate, but actually the solubility is due to the hydrolysis taking place in solution, magnesium hydroxide being a weaker base than is calcium hydroxide. Although there is more than three times as much magnesium as calcium dissolved in sea water, the oceans are not saturated with magnesium carbonate, and its precipitation is more difficult than that of calcium carbonate.

The dolomitic limestones frequently contain some calcite, and all gradations probably exist from calcitic to dolomitic limestones. In many cases, some Mg^{2+} is replaced by Fe^{2+} or Mn^{2+} . Limestones associated with evaporates are usually dolomitic. The dolomitic limestones are partly organogenic in origin, having been formed as shells and skeletons of certain marine organisms. Direct precipitation of dolomite and magnesite may sometimes take place. However, sedimentary magnesites are uncommon.

Dolomites are often formed by diagenesis. Coral reefs are dolomitized as a result of the replacement of CaCO_3 by MgCO_3 . This process has been discussed by Clarke and Wheeler (1922). Aragonite is more readily dissolved than calcite, and it is probable that the aragonitic structures are, at least partly, dissolved away, whereby magnesium carbonate becomes relatively concentrated. Calcite would also be dissolved by the aid of carbon dioxide generated during the decomposition of the organic matter of the organisms, but magnesium carbonate is much less readily removed by this process. On the other hand, a direct replacement of calcium in the aragonite of the coral structures by the magnesium of sea water is also possible. According to Clarke and Wheeler, the solubility of the aragonitic organisms is important as the first stage of the dolomitization, and their replacement is effective in the second stage of the process. However, the actual dolomite ratio between the two carbonates is never

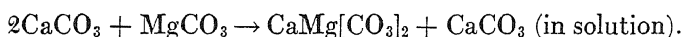
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reached, and it is probable that the formation of dolomite is accomplished only with time, by a series of steps.

Magnesium carbonate may also go into solution as bicarbonate, which is readily soluble above a pH of 9. In more alkaline solutions, only the carbonate ion is present, and, if carbon dioxide is removed by photosynthesis, magnesium carbonate may be precipitated where there is abundant plant life (Atkins, 1930).

When the oxygen contained in marine sediments has been removed in the oxidation of organic matter, magnesium and ferrous iron may start to migrate as bicarbonates. This may lead to the deposition of ferromagnesite, $(\text{Mg,Fe})\text{CO}_3$, in proper surroundings.

Very much dolomite and magnesite is, however, formed by other means than those described above. They are formed from calcitic limestones on a large scale by the metasomatic action of magnesium-rich solutions which replace calcium and form magnesium carbonate:



Dolomitic limestones and magnesites may also originate from igneous rocks rich in magnesium, e.g., pyroxenites and serpentinites, in metasomatic reactions which consist of the replacement of silica by carbon dioxide, whereby carbonates are formed. A part of magnesium is not bound within ferrous minerals during the early and the main stage of magmatic crystallization but remains in the residual liquors. During the pegmatitic stage such remaining magnesium may crystallize in the form of magnesium-bearing minerals, particularly as phosphates and arsenates, but a part still remains in solution right to the hydrothermal stage, during which it will crystallize as magnesite, often in the form of magnesite veins. If the magnesium-bearing hydrothermal solutions come into contact with calcium carbonate, either dolomite or magnesite will be formed, depending on the supply of magnesium which is available. Brucite may also crystallize from hydrothermal solutions in the absence of carbonates.

THE ALKALINE-EARTH METALS: CALCIUM, STRONTIUM, BARIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

THE alkaline-earth metals belong to the second column of the Periodic System. This group also includes radium, which resembles the other members chemically. However, it is radioactive and consequently will be treated separately (see chap. 46). Calcium, strontium, and barium form a very closely coherent group as regards their chemical properties and manner of occurrence in Nature.

The abundance of calcium, strontium, and barium is presented in Table 15.1. The values given in this table are from the following sources: calcium in silicate meteorites from Merrill (1916), recalculated by Goldschmidt (1937*b*); calcium in igneous rocks from Clarke and Washington (1924); strontium in silicate meteorites from Hevesy and Würstlin (1934*b*), recalculated by Goldschmidt (1937*b*); strontium in igneous rocks from Noll (1934); barium in silicate meteorites from von Engelhardt (1936), recalculated by Goldschmidt (1937*b*); barium in igneous rocks from von Engelhardt (1936). In addition, Table 15.1 contains some other abundance values for strontium and barium in igneous rocks; they show the presence of regional differences in the content of these metals in the upper lithosphere, as was suggested by Holmes and Harwood (1932).

Table 2.2 shows that calcium is one of the eight main elements of the upper lithosphere. It is nearly twice as abundant in igneous rocks as in silicate meteorites. In the Sun's atmosphere, however, the abundance of calcium is relatively low. Both strontium and barium are considerably more abundant in igneous rocks than in silicate meteorites, and a comparison of their atomic abundance values shows that they are enriched in the solar atmosphere in relation to calcium (see Table 2.3). The reason is the impoverishment of the solar atmosphere in calcium.

The abundance relationships of strontium and barium are of con-

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siderable interest geochemically. Figure 2.2 shows that the cosmic abundance of elements decreases in accordance with the increase in the atomic number. This rule is valid also with respect to most groups and subgroups of the Periodic System, even though there are some notable exceptions, discussed in chapter 2. According to this rule, the abundance decreases in the following pairs of elements: Rb-Cs, Y-La, Zr-Hf, Cb-Ta. In the pair Sr-Ba, on the other hand, barium is more abundant than strontium in igneous rocks, in respect to both the absolute abundance and the atomic abundance. In silicate meteorites, however, strontium is more abundant than barium, and, according to Figure 2.2, strontium, at any rate, is cosmically more abundant than barium.

TABLE 15.1
ABUNDANCE OF CALCIUM, STRONTIUM, AND BARIUM

MATERIAL	Ca	Sr	Ba
	g/ton		
Silicate meteorites	17,300	26	9
Igneous rocks	36,300	150	250
Plutonic rocks (Hevesy and Wüstrlin, 1934)		110	
Igneous rocks (Tröger, 1934)		300	
Igneous rocks, Dutch East Indies (van Tongeren, 1938)		460	670
Igneous rocks, Sweden (Lundegårdh, 1946)		175	

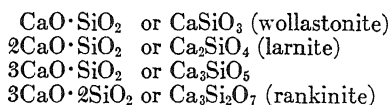
Geochemically, the alkaline-earth metals are strongly lithophile. In meteorites some calcium combines with sulfur and forms the meteorite mineral, oldhamite. However, this compound is not stable in terrestrial surroundings. The formation of oldhamite is due to the fact that the heat of formation of calcium sulfide, and of calcium compounds in general, is relatively high, even higher than the heat of formation of sulfides of other metals present in the meteorites. Therefore, calcium in particular combines with sulfur. Moreover, the redox potential in meteorites is remarkably low, and therefore the calcium sulfide will not be oxidized, as it undoubtedly would be if formed in igneous rocks.

In the upper lithosphere calcium, strontium, and barium are strongly oxyphile.

Owing to its great importance in the biosphere, calcium is a biophile element.

CALCIUM MINERALS

Like magnesium, calcium forms some simple compounds in igneous rocks, but most of its compounds are chemically rather complicated. Referring to the silicates of calcium, the following compounds crystallize in the system CaO-SiO_2 :



All but one of these compounds occur as minerals. The crystal structure of larnite is unknown. The metasilicate, CaSiO_3 , occurs as triclinic wollastonite and monoclinic parawollastonite; the latter is formed from wollastonite by internal twinning. The silicon-oxygen framework of wollastonite consists of independent rings of three Si-O tetrahedra, and consequently the structure of wollastonite is $\text{Ca}_3[\text{Si}_3\text{O}_9]$.

Wollastonite, parawollastonite, and larnite are but rarely formed as primary products of magmatic crystallization. They occur as skarn minerals at igneous contacts in limestones. Larnite is very rare. Therefore, calcium, unlike magnesium, usually is unable to crystallize from rock melts in the form of simple ortho- and metasilicates. The well-pronounced tendency of calcium to form complex silicate minerals with other metals completely dominates its manner of occurrence in igneous rocks.

The most important complex silicates of calcium are the following:

Monticellite,	$\text{CaMg}[\text{SiO}_4]$
Glaucochroite,	$\text{CaMn}[\text{SiO}_4]$
Grossularite,	$\text{Ca}_3\text{Al}_2[\text{SiO}_4]$
Andradite,	$\text{Ca}_3\text{Fe}_2[\text{SiO}_4]$
Uvarovite,	$\text{Ca}_3\text{Cr}_2[\text{SiO}_4]$
Diopside-hedenbergite series	
Augite series	
Hornblende	
Actinolite	
Epidote-zoisite group	
The calcium micas	
Anorthite,	$\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$

The orthosilicates monticellite and glaucochroite and the calcium micas are rare. Margarite, $\text{CaAl}_2[(\text{OH})_2|\text{Al}_2\text{Si}_2\text{O}_{10}]$, and clintonite, $\text{Ca}(\text{Mg},\text{Al})_{3-2}[(\text{OH})_2|\text{Al}_2\text{Si}_2\text{O}_{10}]$, are the most important calcium micas. Owing to their rarity, they do not possess any geochemical importance. Moreover, they are found only in metamorphic rocks.

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The most important carrier of calcium in igneous rocks is anorthite, the pure lime feldspar at the calcium end of the plagioclase series. It belongs structurally to the tectosilicates. Calcium is, in addition, the main metallic constituent of some other tectosilicates, among others, some feldspathoids: cancrinite, $(\text{Na}_2, \text{Ca})_4[\text{CO}_3 | (\text{H}_2\text{O})_{0-3} | (\text{AlSiO}_4)_6]$; and hauynite, $(\text{Na}, \text{Ca})_{8-4}[(\text{SO}_4)_{2-1} | (\text{AlSiO}_4)_6]$; members of the scapolite group; and many zeolites: laumontite, $\text{Ca}[\text{AlSi}_2\text{O}_6]_2 \cdot 4\text{H}_2\text{O}$, heulandite, $\text{Ca}[\text{Al}_2\text{Si}_6\text{O}_{16}] \cdot 5\text{H}_2\text{O}$, and several others. Because the co-ordination number of Ca^{2+} in regard to oxygen (usually 8) is greater than the co-ordination number of Mg^{2+} , the reason being the greater size of the former ion, the incorporation of calcium in the tectosilicate framework results in an electrically neutral structure. Magnesium, on the other hand, cannot form a stable structure. This is the reason why calcium is found in both femic and salic constituents of igneous rocks.

There are several other silicate minerals of calcium of less geochemical importance. Hydrous calcium silicates are known, e.g., hillebrandite, $\text{Ca}_2[\text{SiO}_4] \cdot \text{H}_2\text{O}$, and riversideite, $\text{CaSiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. The borosilicates include, among others, danburite, $\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$, and datolite, $\text{Ca}[\text{OH} | \text{BSiO}_4]$. Melilite, $(\text{Ca}, \text{Na})_2[(\text{Al}, \text{Mg})(\text{Si}, \text{Al})_2\text{O}_7]$, is rather common in some basic igneous rocks. Idocrase (vesuvianite), a complex Ca-Mg-Fe-Al silicate, is common as a contact mineral in limestones.

The most important nonsilicate minerals of calcium are the following:

Calcite, aragonite, vaterite,	CaCO_3
Dolomite,	$\text{CaMg}[\text{CO}_3]_2$
Gypsum,	$\text{Ca}[\text{SO}_4] \cdot 2\text{H}_2\text{O}$
Anhydrite,	$\text{Ca}[\text{SO}_4]$
Fluorite,	CaF_2
Apatite group	

Calcite and aragonite are the two common forms of calcium carbonate. Gypsum and anhydrite are quantitatively important among the evaporate sediments. There are many calcium minerals of more limited geochemical significance. The simple chloride, CaCl_2 , is not found as a mineral because of its high solubility. The complex chloride hydrophilite, KCaCl_3 , occurs as a constituent of some lavas. Prosopite, $\text{Ca}[\text{Al}(\text{F}, \text{OH})_4]_2$, is found in pneumatolytic rocks. Pachnolite and thomsenolite, $\text{NaCa}[\text{AlF}_6] \cdot \text{H}_2\text{O}$, are alteration products of cryolite.

The oxide minerals containing calcium include, among others, perovskite, CaTiO_3 , and a number of columbium- and tantalum-bearing members of the perovskite and pyrochlore groups (see chap.

26). Many calcium-bearing phosphate minerals are known along with apatite. Collophane is a microcrystalline apatite which usually contains F and CO_3 groups. It is the chief constituent of phosphorite. Brushite, $\text{CaH}[\text{PO}_4] \cdot 2\text{H}_2\text{O}$, is a constituent of guano. Autunite, $\text{Ca}[\text{UO}_2|\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$, is a member of the uranite group. There are several arsenates of calcium, e.g., tilasite, $\text{CaMg}[\text{F}|\text{AsO}_4]$, which is isotypic with sphene, and pharmacolite, $\text{CaH}[\text{AsO}_4] \cdot 2\text{H}_2\text{O}$, an alteration product of arseniferous sulfide minerals. Vanadates, molybdates, and tungstates of calcium occur in Nature: rossite, $\text{Ca}[\text{V}_2\text{O}_6] \cdot 4\text{H}_2\text{O}$, and metarossite, $\text{Ca}[\text{V}_2\text{O}_6] \cdot 2\text{H}_2\text{O}$, which occur in some sandstones, are of secondary origin. Scheelite, $\text{Ca}[\text{WO}_4]$, is an important ore of tungsten. Powellite, $\text{Ca}[\text{MoO}_4]$, is the molybdate of corresponding composition. Ankerite, $\text{Ca}(\text{Mg}, \text{Fe})[\text{CO}_3]_2$, is a hydrothermal mineral which is often associated with dolomite.

The calcium-bearing evaporate minerals of marine origin also include glauberite, $\text{Na}_2\text{Ca}[\text{SO}_4]_2$; polyhalite, $\text{K}_2\text{Ca}_2\text{Mg}[\text{SO}_4]_4 \cdot 2\text{H}_2\text{O}$; and tachyhydrite, $2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$. Pirssonite, $\text{Na}_2\text{Ca}[\text{CO}_3]_2 \cdot 2\text{H}_2\text{O}$, and gaylussite, $\text{Na}_2\text{Ca}[\text{CO}_3]_2 \cdot 5\text{H}_2\text{O}$, are important among the calcium-bearing evaporate minerals of closed basins. The calcium-bearing borate minerals are discussed in chapter 16. Other evaporates include nitrocalcite; probably $\text{Ca}[\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$, which is found in many limestone caverns; lautarite, $\text{Ca}[\text{IO}_3]_2$; and dietzeite, $\text{Ca}_2[\text{CrO}_4|(\text{IO}_3)_2]$, which occur in the nitrate deposits of Chile.

CALCIUM IN IGNEOUS ROCKS

The behavior of calcium during normal magmatic differentiation is illustrated by Daly's (1933) analyses quoted in Table 5.32. The early magmatic segregations, which consist chiefly of Mg-rich olivine and enstatite, carry practically no calcium, which remains in the residual melt. Depending on the composition of the melt, calcium sometimes becomes separated during the earliest stage of crystallization in calcic plagioclase. Anorthositic rocks are thereby formed. Starting with the beginning of the main stage of crystallization, much calcium becomes incorporated in the structures of minerals which crystallize from all types of magmas. The content of calcium attains a maximum during the initial steps of the main stage and decreases regularly toward the end of the differentiation.

The relatively early separation of calcium during differentiation is caused by the fact that anorthite becomes stable at a higher temperature than albite. It must be emphasized that during the crystalliza-

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tion calcium is always separated in the form of the aluminosilicate plagioclase, whereas the corresponding calcium-aluminum silicate, grossularite, never forms during the crystallization. As a matter of fact, the minerals of the garnet group are not found in igneous rocks, with the exception of the pyrope-rich garnet of the eclogites. The pegmatites are sometimes garnetiferous, but they contain almandite, which often is relatively rich in manganese. Grossularite is completely irrelevant to igneous rocks, and it is found only as a skarn mineral, that is, in surroundings which are exceptionally high in calcium. The manner of occurrence of plagioclase and grossularite shows that the tectosilicate framework of the plagioclases is considerably more stable than is the nesosilicate framework of the garnets. Because calcium is always able to enter the tectosilicate structure of the plagioclases, no calcium garnet is formed in igneous rocks.

Clarke's (1924) calculations show that the pyroxenes and the amphiboles are the most important femic constituents of igneous rocks (see Table 5.16). Referring to the average calcium content of pyroxenes and amphiboles of dioritic rocks and to the average calcium content of igneous rocks, it may be calculated that approximately one half the total amount of calcium found in igneous rocks is present in the femic constituents and that the other half is contained in the salic constituents (feldspars). The conclusion follows that calcium is incorporated in tectosilicates as readily as in the silicates with chain and ladder structures. The phyllosilicate structure of the micas, on the other hand, is rather uninviting to calcium—a conclusion derived from the rarity of the calcium micas.

According to the discussion presented above, calcium is one of the principal cations in the main constituents of igneous rocks. In addition, it is an important constituent in many accessory minerals, e.g., in apatite, sphene, and fluorite. Apatite and sphene are among the first minerals to crystallize during the formation of igneous rocks, whereas fluorite regularly crystallizes last and fills the interstices between the earlier minerals.

CALCIUM IN THE BIOSPHERE

Calcium is an invariable constituent of all plants. It is essential for the growth of nearly all plants, which contain it both as a structural constituent and as a physiological ion. The Ca^{2+} ion counteracts the toxic effects of K^+ , Na^+ , and Mg^{2+} . Calcium carbonate is important

in regulating the acidity of soil, and therefore it affects the growth of plants.

Calcium is always found in animals, in which it occurs in internal and external skeletal structures, soft tissues, and tissue fluids. The bones of vertebrates contain calcium as tricalcium phosphate, calcium carbonate, and calcium fluoride. In some lower animals the skeletal calcium may be partly replaced by magnesium or totally by silicon. The importance of calcium in animals as a structural constituent is based on its abundance and on the low solubility of the three calcium salts listed above. Calcium is essential in many biological functions of the vertebrates.

The calcium oxalate, whewellite, $\text{Ca}[\text{C}_2\text{O}_4] \cdot \text{H}_2\text{O}$, is common in carbonaceous materials. A calcium citrate, earlandite, $\text{Ca}_3[\text{C}_6\text{H}_5\text{O}_7]_2 \cdot 4\text{H}_2\text{O}$, is also reported to occur in Nature.

CYCLE OF CALCIUM

During chemical weathering the calcium-bearing minerals decompose, and their calcium goes into solution as bicarbonate. However, some calcium is temporarily retained in the zone of weathering as carbonate or sulfate. The content of calcium in the various materials formed during the exogenic cycle is presented in Table 15.2, which is based on information contained in Tables 2.3, 5.52, and 6.7.

The values presented in Table 15.2 show that the content of calcium in the hydrolyzate sediments (shales) is lower than the calcium content in igneous rocks, the difference of the percentages being approximately 1.5. The Na:Ca ratios show no very marked change when the igneous rocks and the shales are compared with each other. Therefore, it is evident that calcium, in analogy to sodium, cannot be notably adsorbed in clays, and consequently the bulk of calcium liberated during the weathering does not become incorporated in the hydrolyzates.

The Na:Ca ratios presented in Table 15.2 emphasize the pronounced difference between river and sea water. Calcium liberated during weathering goes into solution as bicarbonate, $\text{Ca}(\text{HCO}_3)_2$. From this compound calcium is precipitated readily as carbonate, which redissolves with like readiness, and finally all calcium is transported into the sea. Calcium is not precipitated as hydroxide until about $\text{pH} = 11$, and therefore this compound does not exist in Nature. In lake and river waters calcium far exceeds sodium. In the sea, however, their abundance relationship is just the reverse, and sodium

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preponderates. The explanation of the predominance of calcium in river waters is that it is derived, in large part, from limestones and other rocks containing calcium carbonate and from the calcium-bearing salt deposits. These rocks are relatively abundant in the geological column, and, moreover, they dissolve and disintegrate more readily than do the igneous rocks. In addition, among the plagioclase feldspars, which undoubtedly carry the bulk of calcium present in igneous rocks, the calcic members decompose more readily than do the sodic members. Pure albite is chemically more resistant than pure anorthite.

The low content of calcium in the salts dissolved in sea water affords convincing proof of the removal of calcium from the sea. In

TABLE 15.2
CONTENT OF SODIUM AND CALCIUM AND THE Na:Ca
RATIO IN THE MINOR CYCLE

MATERIAL	Na	Ca	Na:Ca
	Per Cent		
Igneous rocks	2 83	3 63	0 78
Dissolved solids in lake and river waters.	5 79	20 39	0 28
Dissolved solids in sea water	30 62	1 15	26 63
Argillaceous sediments (shales)	0 97	2 23	0 43

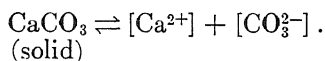
this respect calcium deviates pointedly from sodium, which accumulates in sea water. The comparatively low content of calcium in the hydrolyzates shows that calcium is not deposited therein. It is precipitated, nearly quantitatively, in the carbonate sediments, most of which are precipitates. Calcium is, as a matter of fact, the most important cation of the precipitate sediments. In addition, the marine evaporates are calcium-bearing. They contain calcium usually in the form of sulfate, and only small amounts of double salts, e.g., carbonates, are present. Still another part of calcium may be deposited as phosphate and as fluoride.

CALCITIC LIMESTONES

Calcitic limestones, which may contain more than 90 per cent CaCO_3 , are, along with the highly siliceous sediments, the purest substances produced in Nature during the cycle of weathering and redeposition. In fresh water the deposition of calcium carbonate

probably is almost exclusively caused by the escape of carbon dioxide from water into the atmosphere. Calcium carbonate may also be deposited when aquatic plants consume carbon dioxide from water or from the calcium bicarbonate. Thereby the carbonate becomes deposited, and the deposition, in part, takes place on the plants.

The formation and solution of calcium carbonate constitutes part of the carbon dioxide equilibrium in the sea (see chaps. 6 and 19). Schloesing (1872) was the first to prove, by experiment, that the solubility of calcium carbonate in water depends on the content of carbon dioxide in the gaseous phase in equilibrium with the aqueous phase. Wattenberg (1936) has explained the effect of carbon dioxide on the solubility of calcium carbonate on the basis of the equilibrium which exists between the solid calcium carbonate and the Ca^{2+} and CO_3^{2-} ions found in solution:



The hydrogen ions generated in the dissociation of carbonic acid are largely united with the carbonate ions to produce bicarbonate ions, HCO_3^- , which are only sparingly dissociated. This process disturbs the calcium carbonate equilibrium, and additional calcium carbonate is dissolved until the solubility product of calcium carbonate reaches its previous value; the concentration of the calcium ions increases.

Calcium carbonate removed from sea water forms the bulk of all carbonate sediments. Approximately one-fifth of the total sediments annually deposited in the sea consists of calcium carbonate. According to Kuenen (1941), the recent deep-sea deposits contain about 15 per cent CaO , and all sediments formed contain approximately 12.5 per cent CaO .

The precipitation of calcium carbonate in the sea takes place in many different ways. Some calcium carbonate is precipitated by physical means from colloidal solutions or when the fine calcium carbonate particles carried in suspension settle or when the detrital, coarse-grained calcium carbonate carried to the sea by rivers is deposited.

The quantity of calcium carbonate which may exist in solution in sea water is limited by the solubility of calcium carbonate. When sea water becomes supersaturated with respect to calcium carbonate, precipitation of the excess will take place. The deposition of calcium carbonate is, in part, a purely inorganic phenomenon. However, the

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mechanism of the inorganic precipitation of calcium carbonate and its cycle in the sea are still known incompletely. Johnston and Williamson (1916) pointed out that the surface layers of the warm seas are substantially saturated with calcium carbonate, and, according to Wattenberg (1936), the surface layers of the whole ocean are constantly supersaturated with this compound. The reason is that equilibrium with both atmospheric carbon dioxide and solid calcium carbonate is not attained in the surface layer of the ocean. When the water has attained approximate equilibrium with the carbon dioxide in the atmosphere, the surface layer is in a metastable state with respect to calcium carbonate. On the other hand, if equilibrium has been attained with respect to solid calcium carbonate, when the water is brought into contact with it, calcium carbonate will precipitate, the partial tension of carbon dioxide in water will increase, and part of the carbon dioxide will be given off to the atmosphere. In the metastable state calcium carbonate is precipitated only in the presence of crystallization nuclei. The number of the nuclei in the uppermost layer of the whole ocean is so small that the precipitation necessarily must be very slow. Therefore, the upper layers of the sea endeavor to attain equilibrium with the atmosphere.

In tropical seas the supersaturation may be as high as 300–700 per cent. Equilibrium is attained at a depth of approximately 150 m. The deep waters, beginning with a depth of approximately 2,500 m, contain more calcium carbonate than do the surface waters. This is due to the solution of calcium carbonate from the settling calcareous organisms and from the bottom sediments. If there is an adequate supply of calcium carbonate available, the deeper waters may become completely saturated with it. However, with increasing depth, the water becomes undersaturated, and at great depths it is always undersaturated and consequently able to dissolve calcium carbonate. The red clay is formed as an insoluble residue when calcium carbonate is dissolved from the bottom deposits.

The lower temperature and the increased carbon dioxide content of the deep waters are the cause of the solution of calcium carbonate. The bottom currents carry the calcium bicarbonate in solution to places in which it is reprecipitated, owing to chemical or biological causes. Therefore, the bottom sediments are largely regenerated.

The solubility of calcium carbonate in sea water depends on several factors, viz., temperature, the partial pressure of carbon dioxide in water, the pH, and the content of other dissolved substances. The

solubility of calcium carbonate decreases with increasing temperature and pH and increases with an increase in the partial pressure of carbon dioxide. The solubility decreases if other calcium salts are brought into solution. It increases with an increase in the concentration of other neutral salts in solution. The higher the salinity, the more readily may the water become supersaturated with calcium carbonate.

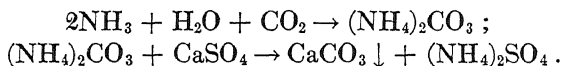
Even small changes in temperature and in the partial tension of carbon dioxide in sea water may have far-reaching effects, as Johnston and Williamson (1916) have shown. They consider a current of sea water, saturated with calcium carbonate at a temperature of 15°C ., which rises to the surface and is slowly warmed. They further presume that the current, after traveling 1,000 km in the sea, is warmed up to 20°C . and that the depth of the current is 100 m and its velocity 27.4 km in 24 hours. The increase in temperature causes a decrease in the solubility of gaseous carbon dioxide, with a subsequent decrease in its content in sea water; and therefore a part of the calcium carbonate is precipitated, which amounts, according to calculations, to 2 mm annually on the strip covered by the current. This corresponds to about $5 \cdot 10^6 \text{ kg} \cdot \text{cm}^{-2}$ annually; the estimate is probably a minimum. The precipitation of calcium carbonate may also take place in a limited area, and therefore the thickness of the deposit is greater than in the previous example. Consequently, it is evident that very notable amounts of calcium carbonate may be locally deposited. The Florida and Bahama marine calcareous deposits, which consist of aragonite, are partly precipitated from sea water saturated with calcium carbonate. However, the calcium carbonate may be redissolved in the deep waters. Therefore, it follows that the inorganic precipitation of calcium carbonate evidently takes place in certain regions of the sea, especially in the supersaturated waters of the lower latitudes, and the precipitated carbonate is redissolved in other areas.

Seasonal changes in the physical and chemical properties of sea water affect the degree of supersaturation with calcite in the sea. According to Buch (1940), water in the northern part of the Baltic, in the Gulf of Finland, and in the Gulf of Bothnia is slightly supersaturated with calcium carbonate during the summer months and absorbs carbon dioxide from the atmosphere. During the fall the degree of supersaturation decreases, and the water gives off carbon dioxide to the atmosphere. The reason is that temperature decreases and the

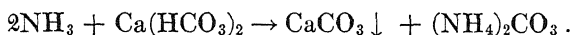
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acid deep waters rise to the surface. During the winter both temperature and pH remain rather stable, and the carbon dioxide system of the sea attains equilibrium with the carbon dioxide in the atmosphere. The water is acid, and it is more undersaturated with calcium carbonate, the lower the salt content is. In the spring the growth of the phytoplankton sets in, assimilation of carbon dioxide starts, and the water grows alkaline. Therefore, the strong undersaturation is gradually compensated.

Micro-organisms may also establish conditions which are favorable for the precipitation of calcium carbonate, particularly in some tropical regions of the sea. However, these micro-organisms are not directly responsible for the precipitation. They produce ammonia, which acts as a precipitating agent. It may cause the precipitation of calcium carbonate directly by increasing the pH, or it may react with carbon dioxide to form ammonium bicarbonate, which then precipitates calcium as carbonate, as follows:



Ammonia may also directly react with dissolved calcium bicarbonate, thus:



In addition, bacteria may decompose organic compounds containing calcium, whereby calcium carbonate is produced by carbon dioxide formed during the decomposition.

On the other hand, carbon dioxide produced during the decay of organic substances may cause the partial solution of calcium carbonate. In like manner, carbon dioxide produced by respiration causes a decrease in pH and solution of calcium carbonate. When proteins are decomposed, ammonia in excess over carbon dioxide may be produced, and thus the solution is rendered basic and calcium carbonate may precipitate. These processes, along with changes in temperature and in partial tension of carbon dioxide, affect the solubility of calcium carbonate and cause recrystallization, by which the calcareous muds are converted into limestones.

Still another manner of formation of the carbonate sediments is directly connected with marine organisms and is of high geochemical importance. Calcium and magnesium carbonate and, partly, calcium sulfate and phosphate are found as constituents of the hard parts of

many marine organisms, both plants and animals. Some analyses showing the chemical composition of the skeletal material of marine organisms were given in Table 8.3. The calcareous remains of marine organisms are important constituents of marine sediments, some of which are nearly totally composed of calcareous material. Fresh-water shells are mostly aragonite, but the skeletal and protective parts of the structures of marine organisms consist either of calcite or of aragonite. Vaterite, the third modification of calcium carbonate, is believed to be the first form of CaCO_3 usually to be formed in the shells of gastropods. It is converted into aragonite, which is unstable in the presence of calcite and water and thus usually does not persist in the sea. However, it is not known whether aragonite is selectively dissolved or whether it is converted into calcite after the death of the organisms. Photosynthetic activity favors the development of calcareous structures by removing carbon dioxide and thereby increasing the concentration of the carbonate ions. It is probable that an increase in the salinity of water affects the organic precipitation of calcium carbonate because the content of calcium carbonate in marine sediments increases with increasing salinity of the surface water (Trask, 1937). The details of the mechanism by which marine organisms separate calcium carbonate are still unknown. Precipitation by organisms does not require the water to be saturated with calcium carbonate. According to Clarke and Wheeler (1922), the algae as limestone-builders are far more important than the corals. The role of pelagic animals is unimportant, but the remains of the bottom fauna, particularly in the lower latitudes, may form an important proportion of the calcareous sediments.

Deposits high in calcareous structures are generally restricted to tropical areas, in which the degree of supersaturation with calcium carbonate is high. More calcium carbonate is separated by organisms in the warm seas of the lower latitudes than in the cold polar seas. Increased temperature favors the replacement of calcium by magnesium in the structures, but at low temperatures strontium seems to substitute for calcium.

Mechanical disintegration also seems to play a role in the deposition of carbonate sediments in the sea. The finely divided calcium carbonate which is found in some deep-sea sediments is believed to be produced from shells of foraminifers. In near-shore waters calcareous shells crushed by wave motion may act as crystallization nuclei.

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Whether the inorganic or the organic processes play the dominating role in the production of the carbonate sediments still remains a matter of controversy. According to Vernadsky (1924), practically all marine carbonate sediments are of organic origin. Several authorities think, however, that the bulk of the limestones are, instead, of inorganic origin, although they often carry notable quantities of calcium carbonate deposited by organisms. At any rate, it seems to be reasonable to assume that, before the Cambrian, calcium carbonate was precipitated by inorganic means and that, thereafter, biological precipitation and accumulation took place on an increasing scale. According to the most recent statements, it is probable that most calcitic limestones are of organic origin (Twenhofel, 1939; Buch, 1946) or that the biogenic limestones are more common than the limestones formed by inorganic processes (Correns, 1943). Although aragonite is precipitated inorganically, its amount is very low (Buch, 1946).

When ground waters and thermal waters ascend to the surface, they often precipitate calcium carbonate as calcite or aragonite. Carbon dioxide contained in the waters is liberated because of release of pressure or agitation, or it is consumed in the biochemical activity of algae, and thereby calcium carbonate is deposited. The sediments formed are called calcareous tufas or sinters and travertines, and they may sometimes form beds of notable extent.

When natural waters evaporate, the dissolved salts are precipitated. Calcium sulfate deposits are found around some springs. Calcium carbonate may be largely deposited before the other dissolved substances separate. Aragonite and calcite are among the first substances to precipitate on evaporation of saline waters. Calcium carbonate is also deposited in caves, largely owing to evaporation. It is also precipitated, along with other salts, from rising ground waters on, or immediately beneath, the surface in arid and semiarid regions.

STRONTIUM AND BARIUM IN IGNEOUS ROCKS

Strontium and barium are among the most abundant trace elements of the upper lithosphere. They are geochemically characterized by the fact that, notwithstanding their relatively high abundance, they only exceptionally form independent minerals in igneous rocks. No independent strontium mineral is known which is formed during the main stage of crystallization. The strontium minerals proper belong to the pegmatitic-pneumatolytic and hydrothermal stages of crystal-

lization, and even in rocks formed during these stages they are rare. The bulk of strontium and barium is concealed in the rock-making minerals of igneous rocks. Although strontium and barium chemically resemble each other and calcium rather closely, their manner of occurrence in igneous rocks shows considerable difference. Strontium accompanies calcium constantly in minerals and rocks of both igneous and sedimentary origin. It also replaces potassium in many minerals, preferably in those of igneous origin, but the strontium-potassium diadochy is not very extensive. Barium, on the other hand, does not generally replace calcium but is extensively substituted for potassium. The reason for the replacement of calcium in igneous rocks by strontium but not by barium is the ionic size. The radii of the ions in question are shown in the accompanying tabulation.

Ion	Radius in kX
Ca ²⁺	1.06
Sr ²⁺	1.27
K ⁺	1.33
Ba ²⁺	1.43

The Ba²⁺ ion is too big to occupy the place of the Ca²⁺ ion in mineral structures, and for the same reason it cannot substitute for Mg²⁺ (radius 0.78 kX) and Fe²⁺ (radius 0.83 kX). On the other hand, the difference between the sizes of Sr²⁺ and Ca²⁺ is considerably smaller. Therefore, strontium, in low concentrations, is more evenly distributed in all igneous rocks than is barium. Both Sr²⁺ and Ba²⁺ may substitute for K⁺ because the radius of K⁺ is intermediate between the radii of the former two ions. Actually, because of the smaller difference in the ionic size, the substitution of potassium by strontium takes place more readily than does the replacement of potassium by barium.

Sr²⁺ may also replace Ba²⁺ in barium minerals and Pb²⁺ (radius 1.32 kX) in some lead minerals. Cerussite may contain as much as 3.15 per cent SrO. However, these possibilities of substitution are of little geochemical importance.

The feldspar structure is undoubtedly the most important habitat of strontium and barium in igneous rocks. Strontium is present both in the plagioclases and in the potash feldspars, but significant amounts of barium are found only in potash feldspar. Eskola (1922) showed that the two metals form artificial feldspars, which are analogous to anorthite. However, only the barium feldspar occurs in Nature as celsian, Ba[Al₂Si₂O₈], and hyalophane, the barium-bearing

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adularia, $(K,Ba)[Al(Al,Si)Si_2O_8]$. The mix-crystals of orthoclase and celsian range continually from $Or_{85}Ce_{15}$ to $Or_{67}Ce_{33}$. Also the strontium feldspar forms a series of isomorphic mixtures with orthoclase. The substitution of K^+ in the feldspar structures by Sr^{2+} and Ba^{2+} is analogous to the Na^+-Ca^{2+} diadochy. Therefore, one may expect that, during the crystallization of potash feldspar, mix-crystals relatively rich in strontium and barium are the first to separate and that pure orthoclase is formed during the later stages of crystallization. Noll (1934) and von Engelhardt (1936) have shown that the content of strontium and barium in potash feldspar really depends on the temperature of formation. The potash feldspars formed during the early steps of the crystallization interval contain, as a rule, more strontium and barium than do the potash feldspars last to crystallize, in which potassium is relatively enriched. The sanidine phenocrysts of volcanic rocks, which were the first minerals to separate during the crystallization, are rich in strontium and barium. Noll (1934) reports the following contents:

Material	Sr (g/ton)
Sanidine from trachyte, Drachenfels, Germany	4,100
Trachyte, Drachenfels, Germany	680

These analyses show that the bulk of the strontium goes into the potash feldspar. According to von Engelhardt (1936), sanidine from trachyte contains a maximum of 14,400 g/ton Ba. However, the abundance of barium in the upper lithosphere is too low to allow the formation of early-crystallizing barium-rich feldspars which would be comparable to the calcic plagioclases, and the analyses given in the accompanying tabulation show that potash feldspar is the chief carrier of barium in igneous rocks (von Engelhardt, 1936).

Material	Ba (g/ton)
Larvikite, Oslo area, Norway	2,100
Augite from larvikite, Oslo area, Norway	27-90
Potash feldspar from larvikite, Oslo area, Norway	2,700-9,000

In the potash feldspars of granite pegmatites and of hydrothermal rocks the content of strontium and barium usually is low. Noll (1934) reports 340 g/ton Sr in adularia, and von Engelhardt (1936) 170 g/ton Ba in amazonite from granite pegmatite. In anorthoclase the content is higher: up to 4,800 g/ton Sr and 6,900 g/ton Ba.

The plagioclase feldspars commonly are strontium-bearing, and

the content of strontium usually is between 0.1 and nearly 1 per cent (Noll, 1934). The reason for the occurrence of strontium in plagioclase is that the strontium feldspar is isomorphic with anorthite. The barium content of plagioclase is rather low: the maximum content is 70–90 g/ton Ba in bytownite (von Engelhardt, 1936).

Muscovite and biotite come next in importance among the barium-containing minerals of igneous rocks. Barium replaces potassium diadochically in the mica structure. Up to 9 per cent Ba may be present in the barian muscovite öllacherite. The barian biotites may contain as much as 6.16 per cent Ba. Strontium, on the other hand, is less readily incorporated in biotite, phlogopite, and muscovite, partly because of their low calcium content. A maximum content of 4,000 g/ton Sr is reported for biotite. According to von Engelhardt (1936), the early-crystallized biotites are rich in barium: a biotite from andesite contains 2,800 g/ton Ba. The content is low in biotites from the late crystallates. In this respect biotite behaves like potash feldspar. Biotite is the chief carrier of barium in diorites and, along with potash feldspar, in alkalic rocks.

The tendency of strontium to replace calcium in mineral structures is, furthermore, shown by its presence in apatite and in the calcium-bearing pyroxenes and amphiboles. The early magmatic apatites, according to Noll (1934), are very much lower in strontium than are the pneumatolytic-hydrothermal apatites because the concentration of strontium in the beginning of the crystallization is very low. Noll's analyses to illustrate this point are given in the accompanying tabulation. The barium content of apatite is low: von Engelhardt found a

AUGITE DIORITE, EGBERSUND, NORWAY

Mineral	Sr (g/ton)
Apatite.....	255
Augite.....	680
Plagioclase.....	~850

content of between 90 and 270 g/ton in this mineral. Up to 940 g/ton Sr is present in pyroxenes and amphiboles (Noll, 1934). The content of strontium in the calcium garnets is low.

Eskola (1922) showed that no artificial strontium silicates exist that are isomorphic with the calcium silicates which also contain magnesium or ferrous iron and that, vice versa, the calcium silicates which are isomorphic with strontium and barium silicates contain no magnesium or ferrous iron. However, in natural calcium-ferromagnesium silicates the replacement of calcium by strontium is possible, as

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the analyses of pyroxenes and amphiboles indicate. According to Wickman (1943), the structure of augite may shrink, owing to the transition of calcium from 8- to 6-co-ordination, and therefore calcium in augite may become substituted by bivalent iron and magnesium but not by barium. In plagioclase, on the other hand, the structure may expand as the co-ordination number increases. Consequently, potassium and strontium, in small amounts, may become incorporated in plagioclase. The co-ordination properties of the potash feldspars are more favorable, and therefore strontium may become enriched in them in relation to calcium.

Strontium and barium cannot replace the rare-earth metals in mineral structures because the substitution of a tripositive ion by a bipositive ion is unfavorable to the stability of the structure in regard to energy relationships. Strontium accompanies the rare-earth metals in many minerals, but it replaces calcium or lead therein. The Sr-TR assemblage also occurs in strontianite, SrCO_3 , but in this mineral the rare-earth metals are captured by strontium.

Sahama and Rankama (1938) found that, as a general rule, the Finnish granites which are rich in the rare-earth metals contain much strontium and relatively much barium. On the other hand, granites which are rich in strontium and barium do not necessarily contain notable quantities of the rare-earth metals.

In alkalic rocks the content of strontium and barium in the potash feldspars may be very considerable. A content of 2.04 per cent Ba is reported in orthoclase from nephelinite. Also in alkalic rocks, strontium and barium concentrate in the feldspar, although small amounts may also be present in the feldspathoids. Noll (1934) found 43 g/ton Sr in nepheline and 255 g/ton in leucite. He published an analysis showing the distribution of strontium in alkalic rocks which is reproduced in the accompanying tabulation. However, in alkalic rocks the

LARDALITE, LÖVE, NORWAY

Mineral	Sr (g/ton)
Biotite.....	8.5
Nepheline.....	85-8.5
Potash feldspar.....	1,700

feldspars of pegmatites formed from residual melts poor in barium also contain less barium. The results of von Engelhardt (1936) indicate a content of 470 g/ton Ba in the potash feldspar of a pegmatitic ditroite.

The alkalic rocks form an exception to the rule that independent minerals of strontium and barium do not occur in igneous rocks formed before the pegmatitic-pneumatolytic stage of crystallization has been reached. The strontium and barium minerals found in alkalic rocks include, among others, the following:

Lamprophyllite, $\text{Na}_3\text{Sr}_2\text{Ti}_3[(\text{O},\text{OH},\text{F}) | (\text{SiO}_4)_2]_2$
 Benitoite, $\text{BaTi}[\text{Si}_3\text{O}_9]$
 Leucosphenite, $\text{Na}_4\text{BaTi}_2[\text{Si}_{10}\text{O}_{27}]$
 Cappelinite, approximately, $\text{Ba}(\text{La}, \dots)_6\text{B}_6[\text{O}_{12}(\text{OH})_2 | (\text{SiO}_4)_3]$

Some other minerals of alkalic rocks also are reported to be rich in strontium. Borowsky and Blochin (1937) found up to 0.5 per cent Sr in zircon and up to 2 per cent in sphene. Apatite contained a maximum of 10 per cent Sr, and 0.6 per cent was present in perovskite. The zirconium silicates may contain material amounts of strontium: 0.4 per cent Sr was found in catapleite and up to 2 per cent in eudialite.

The content of strontium and barium in the various classes of igneous rocks is given in Table 15.3. The analyses show that the basic igneous rocks are the poorest in strontium and barium and that the highest content is found in acidic rocks and, particularly, in alkalic rocks—syenites and nepheline syenites. According to Noll (1934), the syenites, nepheline syenites, and leucite syenites are highest in strontium, but in granitic rocks the enrichment is not striking. A very remarkable fact in the geochemistry of strontium is that volcanic rocks are definitely richer in strontium than are plutonic rocks. Hevesy and Würstlin (1934) found an average of 110 g/ton Sr in plutonic rocks and 330 g/ton in volcanic rocks. Both strontium and barium tend to become concentrated in acidic rocks in regard to calcium. The results of von Engelhardt (1936) show that the highest content of barium is arrived at in alkalic rocks (syenites and nepheline syenites), the reason being the capturing of barium in potash feldspar. The granites, on the other hand, are lower in barium than are the syenites.

In general, the behavior of barium very much resembles the behavior of strontium, and rocks rich in one of the two metals are usually rich in the other as well. However, the content of barium in calc-alkalic rocks increases rapidly toward the granites, whereas the content of strontium changes relatively little during the differentiation.

According to Noll (1934), barium, in relation to strontium, is enriched in rocks carrying potash feldspar. The explanation is that Sr^{2+} ,

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because of its smaller radius, had already become incorporated in mineral structures prior to the crystallization of the potash feldspars. In like manner Shimer (1943) found that barium nearly always predominates over strontium in the feldspars of granites and of granite pegmatites. These observations are quantitatively confirmed by the Sr:Ba ratios given in Table 15.3, which show that strontium is strongly impoverished in relation to barium in granites.

TABLE 15.3
CONTENT OF STRONTIUM AND BARIUM IN IGNEOUS ROCKS

Rock	Sr	Ba	Sr : Ba
	g/ton		
<i>Noll (1934):</i>			
Dunite	0		
German gabbros, composite	170		
German granites, composite	170		
Gabbros (data from literature)	170		
Diorites (data from literature)	260		
Granites (data from literature)	90		
Syenites (data from literature)	600		
Nepheline syenites (data from literature)	1,200		
<i>Hevesy and Wurstlin (1934):</i>			
Peridotites, eclogites, dunites	20		
Ultrabasics	60		
Gabbros	140		
Diorites	170		
Quartz diorites	140		
Granites	120		
<i>von Engelhardt (1936):</i>			
Dunites, pyroxenites		~3	
Gabbros and basalts, anorthosites		60	
Diorites and andesites		230	
Granites and liparites		430	
Greisen		160	
Syenites and trachytes		1,600	
Nepheline syenites and phonolites		520	
<i>Southern Lapland (Sahama, 1945b):</i>			
Ultrabasics	~9	~18	~0.5
Gabbros and dolerites	80	45	1.78
Hetta granites	250	670	0.34
Youngest granites	90	630	0.14
Syenites	570	620	0.92
<i>Rapakivi granites, eastern Fennoscandia (Sahama, 1945c)</i>			
	100	900	0.11
<i>Basic igneous rocks, central Roslagen, Sweden (Lundegårdh, 1946)</i>			
	150		
<i>Acidic igneous rocks, central Roslagen, Sweden (Lundegårdh, 1946)</i>			
	200		

In granite pegmatites the content of strontium and barium is low. However, the two metals, particularly strontium, tend to become concentrated during the last stage of magmatic crystallization: they form independent minerals in hydrothermal rocks. In this respect they behave like calcium, and, in spite of the fact that the bulk of all the three metals is removed from the melt during the main stage of crystallization, they become rather strongly concentrated after the pegmatitic-pneumatolytic stage. The hydrothermal strontium minerals include strontianite, SrCO_3 ; celestite, $\text{Sr}[\text{SO}_4]$; a number of rare complex phosphates and carbonates, e.g., ambatoarinite; probably $\text{Sr}(\text{La}, \dots)[\text{O} | (\text{CO}_3)_3]$; svanbergite, $\text{SrAl}_3[(\text{OH})_6 | \text{SO}_4\text{PO}_4]$; and hamlinite, $\text{SrAl}_3\text{H}[(\text{OH})_6 | (\text{PO}_4)_2]$; and the zeolite brewsterite, $(\text{Sr}, \text{Ba}, \text{Ca})[\text{Al}_2\text{Si}_6\text{O}_{18}] \cdot 5\text{H}_2\text{O}$, which contains up to 8.5 per cent Sr. Other calcium-bearing zeolites may also be rich in strontium, e.g., chabazite with 1 per cent Sr (Noll, 1934). Strontium may also replace calcium in aragonite, calcite, and fluorite of hydrothermal veins. In all these minerals the content of barium, on the other hand, is very low. Aragonite and strontianite are isomorphic and form mix-crystals (calciostrontianite or emmonite). Many barites contain a little strontium. Noll (1934) found about 0.9 per cent Sr in witherite. In thermal waters strontium is enriched in relation to calcium, and its content therein is higher than the content of barium, because barium sulfate is less soluble than strontium sulfate.

Strontianite and celestite are the most important hydrothermal minerals of strontium, but they are not always found in hydrothermal veins. They are much more common in sediments and sedimentary rocks.

The hydrothermal barium minerals include, among others, the following: barite, $\text{Ba}[\text{SO}_4]$, a common constituent in many metaliferous veins; witherite, BaCO_3 ; hyalophane, which is common in dolomite; barylite, $\text{Be}_2\text{Ba}[\text{Si}_2\text{O}_7]$; the zeolites brewsterite (see above), harmotome, $(\text{Ba}, \text{K}_2)_2[\text{Al}_4\text{Si}_{11}\text{O}_{30}] \cdot 10\text{H}_2\text{O}$, and edingtonite, $\text{Ba}[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 3\text{H}_2\text{O}$. In exceptional cases adularia may contain nearly 3 per cent Ba.

The hydrothermal solutions may also extract barium from surrounding rocks. The resulting solutions are enriched in barium in regard to potassium, as they are in calcium in regard to sodium. Thus in the series celsian-potash feldspar and in the series anorthite-albite the component with the higher melting point is preferably attacked and dissolved. The low content of barium in greisen, as compared

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with the content in granites (see Table 15.3), shows that barium is readily removed by fluorine-bearing gases and solutions and becomes concentrated therein, finally giving rise to fluorite-barite veins.

The difference in the ionic size causes the inability of barium to become incorporated in hydrothermal calcium minerals. It forms independent minerals instead. In this respect barium differs from strontium. According to von Engelhardt (1936), the hydrothermal fluorites contain a maximum of approximately 18 g/ton Ba, calcite and aragonite no more than 27–90 g/ton. In strontianite the content may be up to 2,700–9,000 g/ton Ba. Barian aragonite or alstonite and barytocalcite, $\text{CaBa}[\text{CO}_3]_2$, are double salts which barium forms with calcium because, unlike strontium, it cannot become incorporated in the aragonite structure. In some hydrothermal apatites the content of barium may be as high as 0.9–2.7 per cent, but such minerals probably contain admixed barium apatite (von Engelhardt, 1936).

Celestite and barite are the most important ore minerals of strontium and barium. Strontianite and witherite are of minor importance as sources of these metals.

STRONTIUM ISOTOPES

The isotope Sr^{87} , with an abundance of 7.02 per cent, is one of the four stable strontium isotopes. It results in the decay of the radioactive rubidium isotope Rb^{87} (see chap. 12). According to Wickman (1948), the abundance of Sr^{87} in igneous rocks is 20 g/ton; Ahrens (1948*b*) reports a much lower value, viz., 2.5 g/ton. Ahrens found that in many minerals, particularly in those which are formed during the pegmatitic-pneumatolytic stage of crystallization, most of the strontium is radiogenic. In all lepidolites, 80–100 per cent of strontium is radiogenic, and also in amazonite, pollucite, muscovite, biotite, and phlogopite Sr^{87} is always present in significant quantities. Because the proportion of radiogenic strontium sometimes may be appreciable or because this isotope may even predominate in pegmatites and pneumatolytic rocks, their Ca:Sr and Sr:Ba ratios, according to Ahrens, do not necessarily always represent the original ratio of these metals in rocks during the crystallization. However, in most cases when the minerals and rocks formed during the main stage of crystallization are dealt with, the Ca:Sr and Sr:Ba ratios may be applied without the necessity of making corrections from the rubidium content or from the abundance ratio of the strontium isotopes. It

is therefore safe to conclude with Noll (1934) that the Sr:Ca ratio increases toward the end of magmatic crystallization.

Wickman (1948) has shown that the isotope ratio $\text{Sr}^{87}:\text{Sr}^{86}$ may be used to calculate the age of certain marine sediments, e.g., limestones and anhydrites.

STRONTIUM AND BARIUM IN THE BIOSPHERE

Strontium has been found in both terrestrial and marine plants. Usually it is not strongly enriched in plant ashes, but plants growing in soil underlain by celestite-rich sediments are known to be rich in strontium. The content in soil, according to Mitchell (1944), is 50–5,000 g/ton Sr. Sometimes strontium is enriched in coal ashes (Goldschmidt and Peters, 1933c). Dinger (1930) found that plants are able to convert strontium sulfate into carbonate or bicarbonate. In addition, some bacteria may convert strontium and calcium carbonate into bicarbonate, which goes into solution. It has been suggested that organisms cause precipitation of celestite in sediments.

Strontium is a microconstituent of terrestrial animals. In soft tissues its content is low, but it is higher in the bones. However, strontium is not found to replace calcium in bones. Many marine animals, for example, corals, mollusks, and brachiopods, contain strontium. The skeleton of a radiolarian consists entirely or almost entirely of strontium sulfate.

Strontium is probably a fellow-traveler of calcium in the biosphere and does not have notable physiological importance.

Barium is sometimes enriched in the ashes of terrestrial and aquatic plants. In plants it may replace calcium and magnesium. According to Mitchell (1944), the content of barium in soil is 300–5,000 g/ton. In the ashes of oak leaves von Engelhardt (1936) found up to 0.09–0.27 g/ton Ba and 0.027–0.09 g/ton in the ashes of the alga, *Fucus vesiculosus*. A maximum content of 0.9–2.7 g/ton Ba was present in coal ashes.

Barium occurs in both terrestrial and marine animals. However, it is not taken up by animals in significant concentrations. It does not become enriched in the shells of lower organisms; the content is low in the radiolarian and *Globigerina* oozes (see Table 15.4). It is claimed that some rhizopod protozoans contain small granules of barium sulfate in their protoplasm. It is probable that this barium sulfate has been precipitated by organic processes. Barium is able to replace calcium neither in the shells, which consist of calcite and aragonite, nor

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in the bones, which consist of hydroxylapatite. In large doses barium is poisonous to higher animals.

Barium, like strontium, probably is a fellow-traveler of calcium without much physiological importance.

CYCLE OF STRONTIUM AND BARIUM

During weathering, strontium and barium are dissolved as bicarbonates, chlorides, and sulfates. They may migrate as bicarbonate and chloride but also as sulfate. Even though barium sulfate is only sparingly soluble in distilled water, its solubility increases when hydrochloric acid or chlorides of the alkali metals are present in solution. The sulfates and carbonates of strontium and barium are less soluble than the corresponding calcium salts.

Strontium may become precipitated as carbonate through loss of carbon dioxide from the bicarbonate-bearing solution and as sulfate, owing to the action of sulfuric acid or sulfates on the strontium-bearing solutions. However, the bulk of strontium migrates into the sea. According to Table 15.1, the Ca:Sr ratio in igneous rocks is 242, and from Table 6.17 it may be calculated that the ratio in sea water is 30.8. These numbers show that strontium is strongly enriched in sea water in relation to calcium.

The transfer percentage of strontium is 7.2 (see Table 6.19), and consequently strontium is notably concentrated in the sea. It is removed from sea water into the precipitate and evaporate sediments. Some strontium is also extracted, as sulfate, by radiolarians, to be used in their shells. Calcite, dolomite, gypsum, and the potassium salts, among the two groups of sediments mentioned, do not incorporate much strontium to replace calcium and potassium diadochically, because of the relatively low temperature of formation of these minerals—hence the lower degree of diadochic replacement than in minerals crystallizing from the magma at elevated temperatures. Thus, for example, calcite formed during the main stage of crystallization may contain as much as 4,100 g/ton Sr, whereas the sedimentary calcites, like those of hydrothermal origin, are very much lower in strontium (Noll, 1934).

Aragonite and anhydrite are the chief carriers of strontium among minerals formed during the exogenic cycle. Aragonite contains up to 4 per cent Sr (Noll, 1934). The strontium content of gypsum and calcite, although sometimes notable, may be caused by celestite occurring as an impurity. The substitution of K^+ by Sr^{2+} in potassium min-

erals of evaporates is impossible because the electrical balance of the structure cannot be maintained, owing to the lack of suitable anion complexes which could substitute for the chloride and sulfate anions. The bulk of the strontium is separated from the brines during the first stages of their crystallization and goes into anhydrite and polyhalite. According to Noll (1934), polyhalite contains 1,000 g/ton Sr. and anhydrite up to 5,900 g/ton, whereas the content in potassium salts is negligible—about 1.7 g/ton Sr in carnallite and about 0.2 g/ton in sylvite. In gypsum formed by the hydration of anhydrite, the content found by Noll was 1,100 g/ton Sr, but the sample evidently contained strontium sulfate as an admixture.

Contrary to the extreme rarity of strontium minerals in rocks of igneous origin, these minerals are rather commonly formed during the exogenic cycle, even though their number is not high. The minerals in question are celestite and strontianite, the latter of which is rare as a rock-making constituent of sediments and sedimentary rocks. It is usually found only locally in cavities and fissures or in veins in sedimentary rocks. Celestite is nearly always associated with limestones, dolomites, and gypsum-bearing rocks and with minerals of salt deposits. It forms independent grains and crystals in these rocks or is found as intercalated layers therein. This assemblage includes the minerals which do not incorporate considerable amounts of strontium in their structures, and therefore celestite is formed as an independent mineral. The secondary accumulations of strontium in sedimentary rocks are derived from such primary celestite and, further, from strontium found in aragonite and in residual solutions from which calcite and salt sediments crystallize. When aragonite is converted into calcite, strontium is set free and may migrate as sulfate. According to Dinger (1930), the celestite found in sediments and sedimentary rocks is of secondary origin. It is formed by strontium which has migrated as bicarbonate and reacted with gypsum to produce celestite or by strontium mobilized as sulfate in salt solutions.

Celestite is, furthermore, very often associated with remains of marine organisms which have originally built shells consisting of aragonite. These fossils contain up to 4,250 g/ton Sr (Noll, 1934). Noll explained this manner of occurrence as a diadochic replacement of Ca^{2+} by Sr^{2+} in the aragonite structure. Because aragonite is less stable than calcite, it is often converted into calcite or goes into solution, and thereby strontium is separated and precipitated in the fossils as sulfate. Strontianite, on the other hand, is always connected

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with calcareous sediments, consisting of calcite. This manner of occurrence, however, still remains to be explained.

The values in Table 15.4 show the content of strontium and barium in some sediments and their derivatives. The strontium values of the rocks of southern Lapland show that the content of strontium in

TABLE 15.4
CONTENT OF STRONTIUM AND BARIUM IN SEDIMENTS
AND THEIR DERIVATIVES

Rock	Sr	Ba	Sr Ba
	g/ton		
Shales, composite (Noll, 1934)	170		
Limestones (Noll, 1934).	425-765		
Shales and phyllites, av. (Hevesy and Würstlin, 1934) .	20		
Red clay, av. (Hevesy and Würstlin, 1934)	60		
Shales, av. (Noll, 1934)		630	
<i>von Engelhardt (1936):</i>			
Sandstones, av.		170	
Quartzites, av.		110	
Shales, av.		460	
Red clay.		200	
Radiolarian ooze.		~180	
<i>Globigerina</i> ooze		~180	
Minette iron ore.		380	
Limestones, av.		120	
Evaporates, maximum		~9	
Phosphorite, maximum		270-900	
<i>Sahama (1945b):</i>			
Quartzites, southern Lapland, av.	<26	500	<0 05
Aluminum-rich schists, southern Lapland, av. . . .	160	690	0 23
Carbonate rocks, southern Lapland, av.	~850	270	~3 15

rocks of sedimentary origin, with the exception of the carbonate rocks, is usually lower than in igneous rocks. This result affords proof of the high mobility of strontium during weathering.

During metamorphism strontium does not form any new minerals.

Barium may become separated from the weathering solutions as barium sulfate upon evaporation or neutralization (by limestones) of the waters or because of an increase in the concentration of the sulfate anion. Mineral waters contain up to 10-12 g/l barium. Barium sulfate deposited in sandstones and in calcitic and dolomitic lime-

stones may give rise to extensive deposits of barite. Barium may also be precipitated as carbonate from solutions from which carbon dioxide is lost. Under the action of sulfate-bearing waters the bicarbonate solutions precipitate barium as sulfate.

The barium transported to the sea becomes largely separated already during the formation of hydrolyzate sediments, and only a small part thereof remains in sea water, contrary to strontium. The transfer percentage of barium is 0.03, or very much smaller than the transfer percentage of strontium and calcium. The Sr:Ba ratio in igneous rocks is 0.6 and in sea water 260; these values show that barium is strongly impoverished in the sea in relation to strontium. The removal of barium in clays is caused by its greater ionic radius and lower ionic potential, compared with strontium. Therefore, barium is adsorbed in the hydrolyzates more strongly than strontium is, and the argillaceous sediments are the richest in barium. The adsorption of barium in the near-shore clays explains why red clay is comparatively low in barium.

With reference to their adsorption properties, strontium and barium behave like sodium and potassium, which form univalent ions, while strontium and barium form bivalent ions. The ionic radius of K^+ is greater than the radius of Na^+ , and the radius of Ba^{2+} greater than that of Sr^{2+} . Therefore, the ionic potential of K^+ and Ba^{2+} is smaller and the quantity adsorbed by clays greater, compared with the potentials and adsorbed quantities of Na^+ and Sr^{2+} , respectively. Barium is adsorbed so strongly that it has largely been removed in the near-shore sediments, and only a negligible amount is carried to the open ocean, where it is finally precipitated in the deep-sea sediments. In some rare cases marine deposits contain notable amounts of barium as barite concretions and nodules, which may carry as much as 82 per cent $BaSO_4$ and are probably formed by chemical precipitation. Emery and Revelle (according to Sverdrup, Johnson, and Fleming, 1942) explain some of these concretions as results of the interaction of hot-spring water high in barium and of the sulfates of sea water.

Like hydrolyzates, oxidates, particularly the ones rich in manganese, also concentrate barium. The analyses of von Engelhardt (1936) yielded a content of 900 g/ton Ba in a manganese nodule. There is, accordingly, considerable enrichment of barium, in spite of its low concentration in sea water. He also found 1,550 g/ton Ba in a lake iron ore low in manganese and 6,700 g/ton in a manganese-rich sample. Up

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to 8.58 per cent Ba is reported to occur in wad; and hollandite, a barium-containing pyrolusite or polianite, may contain nearly 16 per cent Ba. Barium is enriched in the manganese-rich oxidates because the $\text{Mn}(\text{OH})_4$ sol is negatively charged and thus attracts cations, contrary to the $\text{Fe}(\text{OH})_3$ sol, which is positively charged and attracts anions. In like manner the $\text{Al}(\text{OH})_3$ sol is positively charged. This explains the low manganese content of bauxite, which contains a maximum of approximately 90 g/ton Ba (von Engelhardt, 1936).

The resistates are generally low in barium. The low content of the sandstones and quartzites shows that barium cannot become enriched in clays as precipitated barium sulfate because, if precipitation did take place, the sandstones should also contain more barium than they actually do (see Table 15.4). However, Sahama's (1945*b*) analyses of the rocks of southern Lapland in Table 15.4 show that the quartzites of this area are rather high in barium, and therefore the possibility is not excluded that barium, owing to the low solubility of its sulfate, is deprived of many possibilities of migration in the exogenic cycle.

Table 15.4 also shows that the barium content of precipitates and evaporates is low. In limestones at least a part of the barium content is caused by admixture of argillaceous material. According to von Engelhardt (1936), the low value in limestones is partly caused by the small quantity of barium available during their formation and partly by the absence of the barium-calcium diadochy, which does not exist even at the elevated temperatures of formation of igneous rocks. Like strontium, barium is incorporated in the low-temperature salt minerals only with difficulty. Unlike strontium, which is concentrated in anhydrite and sometimes in gypsum, barium is present in these minerals only in traces, which may be attributed to impurities consisting of argillaceous material. Barium does not form independent minerals in evaporates because of its low content in sea water and in the concentrating brines.

Witherite is sometimes found as a secondary mineral in sediments. Some barium minerals of secondary origin are found in the zone of oxidation, viz., uranocircite, $\text{Ba}[\text{UO}_2|\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$, a member of the uranite group (see chap. 30), and nitrobarite, $\text{Ba}[\text{NO}_3]_2$, which occurs in the nitrate deposits of Chile.

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

IT HAS been repeatedly pointed out on previous occasions that the cosmic abundance of boron, like that of lithium and beryllium, its neighbors in the Periodic System, is conspicuously low. These three elements occupy a deep minimum in all graphic presentations of the abundance of elements (see chap. 2). The estimation of the terrestrial abundance of boron is connected with difficulties arising from the fact that a considerable part of this element is given off by volcanic emanations directly into the hydrosphere. Therefore, its abundance in the upper lithosphere must actually be higher than the value obtained by analyzing igneous rocks shows. The abundance values of boron are presented in Table 16.1.

TABLE 16.1

ABUNDANCE OF BORON

Material	B (g/ton)
Meteoritic iron (Goldschmidt and Peters, 1932c).....	<0.9
Silicate meteorites (Goldschmidt and Peters, 1932c)	1.6
Igneous rocks (Goldschmidt and Peters, 1932c, d)	3
Igneous rocks of Sweden (Lundegårdh, 1946).....	30

The abundance of boron is best elucidated by a comparison with that of hydrogen in volcanic gases (see Table 5.40), in which the atomic abundance ratio B:H is 1:12,500. With reference to the abundance of boron in igneous rocks, the actual value might be higher than that given by Goldschmidt (1937*b*), as pointed out by Lundegårdh (1946). At least, there seem to be considerable regional differences in the boron content of the upper lithosphere. Landergren (1945) has found, on an average, more boron in Swedish granites than in the German granites analyzed by Goldschmidt and Peters (1932c).

In the Sun's atmosphere the presence of boron is still not definitely established.

The general geochemical character of boron is that of a lithophile

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element. With reference to its terrestrial occurrence, boron is also notably biophile.

BORON IN IGNEOUS ROCKS

In the upper lithosphere boron is always combined with oxygen. It is therefore a typically oxyphile element. The content of boron in some more important groups of igneous rocks is presented in Table 16.2. The values reported show that boron, like beryllium, is an element characteristic of the late stages of magmatic crystallization. During the main stage of crystallization some minerals, such as biotite and the amphiboles which have hydroxyl groups in their structures, may incorporate small amounts of boron. Therefore, boron is

TABLE 16.2
CONTENT OF BORON IN IGNEOUS ROCKS

Rock	B (g/ton)
Basalts, average (Goldschmidt and Peters, 1932 <i>d</i>).....	1.6
Composite of German gabbros (Goldschmidt and Peters, 1932 <i>c</i>).....	3
Composite of German granites (Goldschmidt and Peters, 1932 <i>c</i>).....	3
Liparite (Goldschmidt and Peters, 1932 <i>d</i>).....	31
Nepheline syenites, average (Goldschmidt and Peters, 1932 <i>d</i>)	3
<i>Rocks of the Basement Complex of southern Lapland (Sahama, 1945<i>b</i>):</i>	
Ultrabasics.	31
Gabbros and dolerites	9
Granites.....	0.9-3
Syenites	9

often present in some basic rocks, e.g., gabbros. Goldschmidt and Peters (1932*d*) have found 16 g/ton B in a pneumatolytic hornblende and 3 g/ton B in a biotite from granite pegmatite. Relatively large amounts of boron may be present in the ultrabasic serpentine rocks (Sahama, 1945*b*), which are usually thought to be formed from dunite in autometamorphic processes. The boron content increases parallel with the increase in the content of serpentine. It seems to be evident that boron, when present in these rocks, was originally enriched in the aqueous solutions resulting from the crystallization of the ultrabasics. Boron, however, did not enter the fractions lowest in silica but was introduced into the serpentine during the autometamorphism.

The boron content of magmatic iron ores is very low. Goldschmidt and Peters (1932*d*) report a maximum of 1.6 g/ton B. According to Landergren (1945), boron is enriched in the manganiferous iron ores

of Sweden, those containing braunite being the highest in this element.

The small ionic size of boron (the radius of the B^{3+} ion is 0.20 kX) and the volatility of many of its compounds, however, prevent its becoming totally trapped in the hydroxyl-bearing minerals during the magmatic crystallization. The bulk of boron is enriched in residual magmas and solutions and will sometimes crystallize as independent boron minerals even during the last phases of the main stage of crystallization. Usually, however, no boron minerals will crystallize until the pegmatitic and even hydrothermal stages are reached.

Tourmaline, with 9–11.5 per cent B_2O_3 , is the most important and the most abundant of the boron minerals. The basic rocks do not contain tourmaline, but it is a constituent of granites (tourmaline granites) representing the last products of the main stage of crystallization. In the granites tourmaline has generally crystallized after the feldspars, and it is one of the most conspicuous constituents of pegmatites. In metalliferous hydrothermal formations it belongs to mineral assemblages representing comparatively low temperatures of crystallization. The presence of tourmaline in metalliferous and quartz veins affords proof of the high mobility of boron. This element may easily migrate far from its original source.

Tourmaline may be considered a mixture of the following components:

1. Lithian tourmaline, $NaAl_3LiB_3[O,OH,F|SiO_4]_6 \cdot (OH)_{0-2}$
2. Magnesian tourmaline, $NaAl_5Mg_4B_3[O,OH,F|SiO_4]_6 \cdot (OH)_{0-2}$
3. Aluminian tourmaline, $NaAl_9B_3[O,OH,F|SiO_4]_6 \cdot (OH)_{1-2}$

Magnesium may be replaced by ferrous iron, and sodium by calcium. Sometimes there occur small amounts of potassium, chromium, and titanium. The black iron-rich tourmalines (schorlite) are evidently the most common type.

Boron is present in igneous rocks and also in the late magmatic products of crystallization in the form of numerous boron-bearing silicates and borosilicates. They include, among others, the following species:

Axinite,	$Ca_2(Mn,Fe)Al_2BH[SiO_4]_4$
Dumortierite,	$Al_4[Al_4BSi_3O_{19}OH] (?)$
Danburite,	$Ca[B_2Si_2O_8]$
Datolite,	$Ca[OH BSiO_4]$

Axinite (4.5–6.5 per cent B_2O_3) and datolite (20–22 per cent B_2O_3) are found mainly in basic rocks, such as basalts and diabases. All

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these minerals, however, are comparatively rare and, as compared with tourmaline, of little geochemical importance. The structure of dumortierite is still not known with certainty. Datolite and danburite are real borosilicates, in which boron forms $[\text{BO}_4]$ tetrahedra in a framework composed of $[\text{SiO}_4]$ tetrahedra. Accordingly, boron replaces silicon in the oxygen tetrahedra. As in the case of aluminum and silicon, so with boron and silicon the degree of substitution remains small, because of the considerable difference in the size of the ions concerned ($r_{\text{B}^{3+}} = 0.20 \text{ kX}$; $r_{\text{Si}^{4+}} = 0.39 \text{ kX}$). It is probable that, when the amount of boron during the crystallization is too low to allow the formation of independent boron minerals, it will replace silicon in the $[\text{SiO}_4]$ tetrahedra. Because the greatest part of boron in the upper lithosphere is concealed in the structures of silicate minerals, the foregoing manner of occurrence of boron is of geochemical importance.

Wasserstein (1943) has found very substantial contents of boron in braunite, $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ (up to 1.1–1.2 per cent B_2O_3 in South African occurrences), and he suggests that this mineral is the exclusive carrier of boron among the manganese minerals. The explanation of the occurrence of boron in braunite is probably the diadochic replacement of Si^{4+} by B^{3+} .

BIOGEOCHEMISTRY OF BORON

Boron is physiologically important in plants. It is essential for higher plants, being necessary for their development. Boron is also important to the soil bacteria and promotes the nitrification. It is strongly concentrated by many living plants, and its content may run high in their ashes. Some plants may concentrate boron heavily, even from soil low in this element. According to Goldschmidt and Peters (1932d), soils formed by weathering of igneous rocks are lower in boron (maximum content 3 g/ton B) than the coastal soils and those derived from marine sediments (up to 31 g/ton B). As a matter of fact, boron is notably concentrated from sea water in the coastal soils, which may contain from ten to fifty times as much boron as inland soils do. Boron is also strongly concentrated in coal ashes, the maximum being 3,100 g/ton B (Goldschmidt and Peters, 1932c). These authors report a similar content of boron in the ashes of seaweeds (*Fucus vesiculosus* and *Laminaria saccharina*), whereas the content in marine calcareous algae is less.

Boron is also present in animals. Some corals contain up to 310

g/ton B in their calcareous structures. Still higher contents are reported in siliceous sponges, which may contain up to 1,550 g/ton B in their ashes (Goldschmidt and Peters, 1932*d*). In higher animals the content of boron tends to be low, and it is probably not essential for these animals; in fact, large doses of boron are toxic.

Tageeva (1942) found boron substantially enriched in oil-field waters. This boron is probably ultimately derived from organic substances.

More boron is present in salt-water sapropel than in fresh-water sapropel, according to Guliaeva (1942). In the former case the increase in the content of boron is parallel to the increase in the content of organic matter. No appreciable enrichment of boron, on the other hand, occurs in the fresh-water sapropel. Especially large amounts of boron are present in algal sapropel, which is composed largely of fats (balkhashite). Guliaeva suggests that such algae concentrate boron, which is given back to the surrounding medium during the decay of the organisms. Consequently, salt-water organisms are evidently actively involved in the cycle of boron.

CYCLE OF BORON

The cycle of boron is presented in Figure 16.1, which is based mainly on a paper of Landergren (1945). During magmatic crystallization, boron is partly incorporated in igneous rocks, but a part wells out in volcanic emanations, which are comparatively rich in this element (see Table 5.40). According to Tageeva (1942), mineral waters connected with volcanic activity are high in boron, and Zies (1929) has found as much as 2.17 per cent B_2O_3 in the incrustations in the Valley of Ten Thousand Smokes in Alaska. At elevated temperatures boron is discharged from the magma directly into the atmosphere, but at lower temperatures the hydrothermal solutions deliver it directly into the hydrosphere. In the first case boron is carried into the hydrosphere by condensation. During the chemical weathering of rocks boron goes into solution as boric acid and soluble borates and is ultimately transported into the sea. During mechanical disintegration it is deposited in the resistates. The boron content of the continental weathering products rich in alumina (kaolin, bauxite) is rather low, often still less than in igneous rocks. The reason is the partial leaching-out of boron during the weathering.

In sea water boron is apparently present as undissociated boric acid, which plays an important part in the buffer mechanisms of the

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sea, being second only to the carbonate system. The boron present in sea water is precipitated into hydrolyzates, oxidates, and evaporates, from which it may again be dissolved, at least partly, during the weathering. The boron may then be retransported into the ocean or become concentrated in closed basins on the continents and finally be deposited as borate beds in arid regions.

According to Sahama (1945*b*), boron might be precipitated in the sea as relatively insoluble calcium and magnesium borates, or there might occur exchange reactions to combine borates of these metals

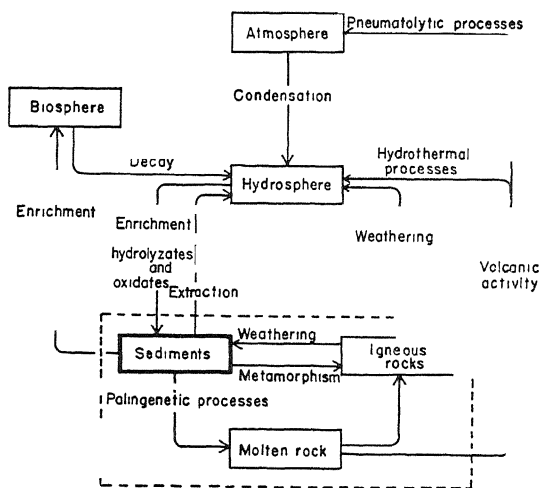


FIG. 16.1.—The cycle of boron

and of aluminum and iron with the hydrolyzates and oxidates. However, according to Landergren (1945), boron in the sediments occurs in a relatively readily volatile form.

During the metamorphism the boron present in the sediments either remains in the recrystallized rocks or goes into the regenerated rock melt formed during the anatexis. Another feature characteristic of the cycle of boron is the transportation of boron from the lithosphere into the biosphere, where it may become considerably enriched. During the decay of the concentrating organisms, boron is liberated and ultimately finds its way back to the hydrosphere. As a matter of fact, the cycle of boron centers around the hydrosphere.

The content of boron in sediments and sedimentary rocks is illustrated by the values presented in Table 16.3. The values show that, compared with marine sediments, igneous rocks and the continental

sediments formed by their disintegration are comparatively low in boron. The bulk of boron is present in marine hydrolyzates and partly in the hydrosphere itself. As pointed out in chapter 5, boron, according to its ionic properties, is an element of the hydrolyzates (Wickman, 1944). The marine oxidates are also rich in boron; Goldschmidt and Peters (1932*d*) found that the iron ores deposited in fresh water are essentially lower in boron than are those of marine

TABLE 16.3

CONTENT OF BORON IN SEDIMENTS AND THEIR DERIVATIVES

Rock	B (g/ton)
Bauxite and kaolin (Goldschmidt and Peters, 1932 <i>d</i>) . . .	max. 3
Laterite-bauxite iron ores (Landergren, 1948)	20
Bog ores, Finland (Goldschmidt and Peters, 1932 <i>d</i>)	0-3.1
Bog ores, Finland (Landergren, 1948)	29
Glauconitic sandstone (Goldschmidt and Peters, 1932 <i>d</i>) .	155
Terrigenous muds (Goldschmidt and Peters, 1932 <i>d</i>) . . .	16-155
Recent marine clays (Goldschmidt and Peters, 1932 <i>d</i>) . .	93
Bottom sediment, Tyrrhenian Sea (Landergren, 1948) . . .	50
Radiolarian ooze, <i>Globigerina</i> ooze, red clay, manganese nodule (Goldschmidt and Peters, 1932 <i>c, d</i>)	155
Shales, average (Goldschmidt and Peters, 1932 <i>c</i>)	310
Sedimentary marine iron ores (Goldschmidt and Peters, 1932 <i>d</i>)	max. 310
Glauconite, Scania (Palmqvist, 1935)	300
Siderite, Scania (Palmqvist, 1935)	160-30
Marine oolitic-siliceous iron ores (Landergren, 1948) . . .	73
Marine siderite ores (Landergren, 1948)	28
Calcitic and dolomitic limestones, average (Goldschmidt and Peters, 1932 <i>d</i>)	3
Quartzites, southern Lapland (Sahama, 1945 <i>b</i>)	9-31
Aluminum-rich schists, southern Lapland (Sahama, 1945 <i>b</i>)	9-93
Carbonate rocks, southern Lapland (Sahama, 1945 <i>b</i>) . . .	9

origin. The average found by Landergren (1948) for the bog ores from Finland is not so low as might be expected, taking into account their lacustrine nature. Landergren suggests that boron might here be of organic origin.

The values given in Table 16.3 show that the boron content in limestones is considerably lower than in argillaceous sediments. In dolomites the content may sometimes be higher, the cause being the marine deposition. Mitchell (1944) has analyzed a large number of limestones from Scottish localities; the content of boron was commonly less than 10 g/ton. Like the limestones, the siliceous sediments are also usually low in boron. This element is absent in diatomite and siliceous sinter (Goldschmidt and Peters, 1932*d*).

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Table 16.3 shows, further, that the siderites are lower in boron than the glauconites are. The low boron content in the bottom sediment from the Tyrrhenian Sea is caused by the relatively high carbonate content of this sediment (Landergren, 1948).

The boron of marine sediments is very largely obtained from sea water. The values presented in Table 6.19 show that boron, like sulfur and chlorine, is strongly concentrated in sea water. The calculations show that the amount of boron now present in sea water is 2.5 times as high as the quantity supplied to the oceans during the geological history of the Earth. According to Goldschmidt and Peters (1932*c, d*), the accumulation of boron in the sea is one of its most conspicuous geochemical features. These authors suggest that the boron of the ocean was largely contained in the protoatmosphere of the Earth as a volatile boron compound, perhaps as the trichloride BCl_3 , and that additional amounts were delivered by volcanic activity during the geological history of the Earth. According to the calculations presented by Goldschmidt (1937*b*), the geochemical balance of boron is illustrated in the accompanying tabulation. The values show that

	B (g)
Hydrolyzate sediments ($155 \text{ kg} \cdot \text{cm}^{-2}$)	25
Sea water ($278.1 \text{ kg} \cdot \text{cm}^{-2}$)	1.2
Total	26.2
Igneous rocks ($160 \text{ kg} \cdot \text{cm}^{-2}$)	0.5

the quantity of boron contained in the hydrolyzates and in the sea is 52.4 times as high as the amount present in igneous rocks.

It was pointed out previously that the resistates nearly always carry considerable amounts of boron, which are chiefly due to the accumulation of tourmaline in the weathering residues. Tourmaline is a mineral very stable against mechanical and chemical denudation (see chap. 5). Tourmaline is the common form of boron in all rocks of sedimentogenic origin, which are originally deposited in the sea. The formation of tourmaline in the derivatives of marine sediments includes the removal of a part of boron from the cycle of the soluble boron compounds.

The preceding discussion shows that boron is definitely thalassophile. This characteristic may allow important conclusions to be drawn concerning the origin of certain metamorphosed rocks in Archean and other terranes. In the case of highly metamorphic rocks, their boron content might often decide their originally igneous or

sedimentary nature. Even though boron in the contact zones of granites frequently originates from the granite magma, being metasomatically added to the surrounding rocks, one must, according to Goldschmidt and Peters (1932*c*), always reckon with the possibility that the boron present in the contact zone in a sedimentogenic rock penetrated by granite intrusions was originally present in the sediment and was later concentrated at and near the granite contact as a result of its high mobility.

The changes in the boron content of the ocean were investigated by Landergren (1945). According to his results, the content of boron in argillaceous sediments is directly proportional to the salinity of the water in which the sediment was deposited. The higher the salinity, the greater the boron content of the accumulated sediments. The ratio between the salinity and the boron content has remained unchanged since at least the Cambrian and probably long before that time. A gradual decrease in the boron content of sea water, as suggested by Goldschmidt and Peters (1932*d*), should therefore not be effective. Because the boron content of marine sediments is considerably higher than that of igneous rocks, it is evident that boron has accumulated in the marine sediments during the course of geological time. The hydrosphere has thus been deprived of twenty to forty times the present quantity of boron in ocean water. At the dawn of the geological history of the Earth the boron content of the ocean must have been considerably higher than at present because during those remote times the volcanic activity was more plentiful and the quantity of the emanations larger than nowadays. As soon as the processes of weathering and the formation of the sediments started, boron became rapidly accumulated in the sediments. The amount of boron dissolved in the ocean diminished quickly until the present, nearly constant, value was attained. The changes in the boron content of sea water are presented in Figure 16.2, which is reproduced from Landergren (1945).

The constancy of the boron content in the ocean water since Cambrian or still older times is due to the equilibrium between the processes which remove boron from the sea and those which introduce additional boron into the oceans. The boron-bearing sediments deposited in the sea must release, directly or indirectly, a part of their boron through the minor (weathering) and the major cycles (volcanic emanations) back to the ocean (see Fig. 16.1). The ocean therefore acts as a vast boron reservoir in the boron cycle. The equilibrium between

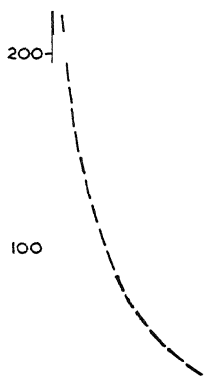
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these two processes was attained long before the beginning of the Cambrian time.

BORON IN EVAPORATES

Boron of two kinds of origin is found in the evaporates. Notable amounts of boron are present in marine evaporates and in evaporates deposited in closed basins as various borates which often occur to-

B_2O_3 in sea
water, g/m³
300—

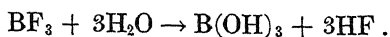


Cambrian Recent

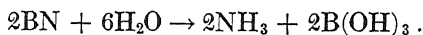
FIG. 16.2.—Changes in the boron content of sea water during the geological evolution of the Earth.

gether with other salt minerals. In addition, borates are found in evaporates connected with volcanic activity.

The boron of volcanic emanations accumulates in the neighborhood of the centers of volcanic and thermal activity as sublimates consisting of boric acid [sassolite, $B(OH)_3$] and various borates. Boric acid is volatile with steam even at 100° C. Readily volatile boron halogenides, such as BCl_3 and BF_3 , may also originally be present in volcanic gases. They produce boric acid in reaction with water vapor, e.g.,



The fumaroles of the area of extinct volcanoes in Tuscany in Italy, an important source of boron, deposit sassolite, larderellite, $\text{NH}_4\text{B}_5\text{O}_8 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, a number of calcium borates, and other boron minerals. The chemical composition of larderellite is of interest, for it is an ammonium borate. Clarke (1924) emphasized the fact that ammonium salts nearly always accompany boron minerals in volcanic sublimates. It should also be noticed that water vapor is quantitatively the most important constituent of volcanic gases. The joint occurrence of boron and nitrogen in volcanic sublimates led Clarke to the hypothesis that boron was originally contained as the nitride, BN, in the volcanic gases. He suggested that this compound is decomposed, owing to the action of water vapor, whereby ammonia and boric acid are formed:



However, according to Schlüter (1928), the boron nitride hypothesis is not based on adequate facts.

The basins of many lakes in the different parts of the world contain notable deposits of borate minerals. The borate beds of southern California and Nevada in the United States contain the following boron minerals as the most important constituents:

Kernite,	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
Borax,	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Ulexite,	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
Colemanite,	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

About 95 per cent of the world's boron is produced in California.

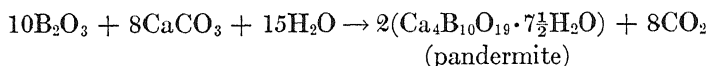
Borate deposits of a similar nature are met in South America in Argentina, Bolivia, Peru, and, particularly, Chile. The most important boron mineral of these deposits is ulexite. Typically, nitrates occur accompanying the borates in the deposits of the Western Hemisphere. Other borate deposits of technical importance are found in Tibet, Persia, and Turkey, most of them being connected with thermal activity and containing ammonium salts.

The boron minerals deposited in closed basins are chiefly calcium borates. This geochemically important fact was explained by Clarke (1924) as a result of the low solubility of the borates of calcium. This metal is the most important cation in lake and river waters. Therefore, boron is precipitated as calcium borate in the presence of soluble calcium salts.

Schlüter (1928) has offered an explanation concerning the origin

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of the borate deposits at Sultan Tshair in Turkey. The chief constituent of these deposits is pandermite (priceite), $\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\frac{1}{2}\text{H}_2\text{O}$. The pandermite layers occur, together with gypsum, as intercalated beds in fluvial sediments, being deposited with these sediments. Boron was produced by late Tertiary igneous activity, and the boron-bearing thermal waters were mixed with river water. The boric acid and the calcium carbonate dissolved in river water reacted to form pandermite according to the equation:



The volcanic activity released carbon dioxide, which was instrumental in increasing the content of calcium, as bicarbonate, in the river water. Concentrated solutions of calcium carbonate were consequently available, and pandermite, not being readily soluble, was precipitated together with gypsum as a separate horizon in the fluvial sediments.

All North and South American borate deposits are fresh-water evaporates, and boron in these beds is evidently genetically connected with the geologically young volcanic rocks found in the neighborhood of the deposits. Because appreciable amounts of boron are present in sea water, boriferous strata are also formed during the deposition of marine evaporates. Thus, for example, the classical salt beds of Stassfurt in Germany, which once crystallized from the Permian Zechstein Sea, contain boron salts in certain horizons, mostly in the carnallite zone. The following boriferous minerals are found in these beds:

α -boracite and β -boracite,	$\text{Mg}_6[\text{Cl}_2 \text{B}_{14}\text{O}_{26}]$
Pinnoite,	$\text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$
Ascharite,	MgHBO_3
Kaliborite,	$\text{KMg}_3\text{B}_{11}\text{O}_{19} \cdot 9\text{H}_2\text{O}$
Hydroboracite,	$\text{CaMgB}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$
Sulfoborite,	$\text{Mg}_3[\text{SO}_4 \text{B}_2\text{O}_5] \cdot 4\frac{1}{2}\text{H}_2\text{O}$

Unlike the closed basins in which calcium borates are deposited, the Stassfurt salt beds contain chiefly magnesium borates. According to Clarke (1924), this is the general rule with reference to marine evaporates. This difference in the composition between marine and fresh-water borate sediments is explained by Clarke as the result of the predominance of magnesium over calcium in sea water; the case is the opposite in lake and river waters. According to Table 6.7, the average composition of dissolved solids in fresh water and in the sea

and the corresponding Mg:Ca ratios are as given in the accompanying tabulation.

	Mg (Per Cent)	Ca (Per Cent)	Mg:Ca
Dissolved solids in lake and river water.	3.41	20.39	0.17
Dissolved solids in sea water	3.69	1.15	3.21

During the evaporation of sea water, calcium salts are precipitated prior to the magnesium salts. Therefore, hydroboracite was the first boron compound to crystallize from the brines of the Zechstein Sea. Like calcium borate, magnesium borate also is only sparingly soluble in water. The borates of certain rare trivalent elements, e.g., indium, scandium, and lanthanum, are insoluble, and therefore it might be possible that such compounds would, at least partly, be responsible for the precipitation of these metals in certain marine sediments. On the other hand, such borates might be incorporated in marine carbonate sediments because, as shown by Goldschmidt and Hauptmann (1932), the orthoborates of scandium and indium are isomorphic with calcite, and the orthoborate of lanthanum is isomorphic with aragonite.

ALUMINUM

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

ACCORDING to Table 2.3, aluminum is the most abundant metal found in igneous rocks. Of all the elements, only oxygen and silicon are more abundant than aluminum. If the cosmic abundance is considered (see Fig. 2.2), iron and magnesium are found to be more abundant than aluminum. As emphasized by Eskola (1946), this fact affords important proof of the origin of the lithosphere by an extensive differentiation process (see chap. 2). The atomic number of aluminum is odd ($Z = 13$), and consequently this metal, according to the rule of Oddo and Harkins, should be less abundant than its neighbors, magnesium and silicon. Such is not the case in igneous rocks, and, consequently, aluminum evidently must have been strongly concentrated in the upper lithosphere. This means that a pronounced chemical differentiation has occurred in the Earth.

The higher cosmic abundance of magnesium is readily understood if its manner of occurrence in the meteorites is considered. The abundance of both magnesium and iron in meteorites is considerably in excess of that of aluminum, because iron is the principal constituent of iron meteorites and stony-irons and because the silicates of the stony meteorites consist chiefly of those of magnesium.

The abundance of aluminum in igneous rocks and in the meteorites is presented in Table 17.1.

In the solar atmosphere the abundance of aluminum is considerably lower than that of magnesium and silicon (see Table 2.3), and the case is thus similar to the abundance relationships of the three elements in the meteorites.

The abundance values recorded in Table 17.1 show that aluminum, like the alkali metals and the alkaline-earth metals, is a thoroughly lithophile element. It is evident that aluminum is practically completely absent in the deeper-lying geochemical shells of the Earth. It is almost quantitatively concentrated in the lithosphere, the highest content being found in the uppermost parts, i.e., in the Sial crust.

ALUMINUM IN IGNEOUS ROCKS

In the upper lithosphere aluminum is a pronouncedly oxyphile element. It is always combined with oxygen; no sulfide minerals of aluminum are known to exist.

The tendency of aluminum to become concentrated in the uppermost lithosphere is reflected also by its behavior during magmatic differentiation. Noteworthy quantities of aluminum are not present in the early products of crystallization. In the early crystallates, aluminum occurs as an essential constituent only in the plagioclase feldspars of anorthosites and in the spinels. The spinels were previously interpreted as aluminates, in which aluminum might be replaced by ferric iron and chromium; but X-ray diffraction studies reveal their character as double oxides, containing either Al_2O_3 , Fe_2O_3 ,

TABLE 17.1
ABUNDANCE OF ALUMINUM

Material	Al (Per Cent)
Meteoritic iron (Noddack and Noddack, 1930)	0.004
Silicate meteorites (Merrill, 1916)	1.79
Igneous rocks (Clarke and Washington, 1924)	8.13

or Cr_2O_3 as one of the component oxides. However, the spinels are quantitatively insignificant as rock-making minerals, and therefore their importance in the geochemistry of aluminum is very small. The scarcity of aluminum in the early crystallates is shown in Daly's (1933; see Table 5.32) averages by the low aluminum content of dunites. Even in the hornblendites, which can no longer be included among the early crystallates, the content of aluminum is considerably lower than in the rocks separated during the main stage of crystallization. In this stage aluminum is somewhat enriched in the first rocks to crystallize, but, with progressive differentiation, its content decreases. Thus, e.g., the average aluminum content of gabbros is higher than that of silicic rocks.

The feldspars, which are quantitatively the most important constituents of igneous rocks, are aluminosilicates of certain univalent and bivalent metals. Therefore, they carry the bulk of the lithospheric aluminum. Although some trivalent metals theoretically may replace aluminum in the feldspar structure, the degree of such substitution in the feldspars is too insignificant to be of much geochemical importance.

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The theoretical aluminum content of the most important feldspars is given in the accompanying tabulation.

Mineral	Al (Per Cent)
Orthoclase and adularia, $K[AlSi_3O_8]$	9.69
Microcline and sanidine, $(K,Na)[AlSi_3O_8]$	(9.69)
Albite, $Na[AlSi_3O_8]$	10.29
Anorthite, $Ca[Al_2Si_2O_8]$	19.40

Anorthite contains double as much aluminum as do albite and the potash feldspars. Consequently, in basic igneous rocks the plagioclase feldspars, which always are relatively rich in the anorthite component, contain more aluminum than do the albite-rich plagioclases and the potash feldspar of acidic rocks. This explains why aluminum is enriched in the early products of the main stage of magmatic differentiation.

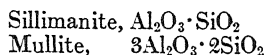
In the alkalic series the syenites and nepheline syenites contain more aluminum than do the calc-alkalic rocks with a corresponding silica content. This is due to the presence of abundant sodic feldspar and feldspathoids among their major constituent minerals; nepheline, leucite, and cancrinite contain more aluminum than potash feldspar does.

Along with the feldspars, the micas contain aluminum as one of the major constituents. Geochemically, biotite is the most important member of the mica group; muscovite is somewhat less important. The different biotite varieties carry from 10 to 20 per cent Al_2O_3 ; this content is of the same order of magnitude as the average alumina content of igneous rocks, calculated by Clarke and Washington (1924; see Table 2.1). Muscovite and allied micas, on the other hand, contain considerably more alumina, sometimes in excess of 30 per cent. Muscovite is an essential constituent almost only in granitic rocks and is nearly always absent in the more basic rocks. Biotite crystallizes prior to muscovite and may therefore become separated from water-rich magmas at a comparatively early stage. Therefore, the presence or absence of biotite does not notably affect the alumina content of igneous rocks, whereas, if muscovite is present, the aluminum content will somewhat increase in rocks crystallized toward the end of the main stage of differentiation. However, the effect of muscovite is less pronounced than that of the feldspars. Moreover, in granites the bulk of muscovite, if not all, is of secondary origin, being a product of the alteration of the feldspars.

The pyroxenes and amphiboles, particularly augite and horn-

blende, which are the most important members of these mineral groups, are regularly aluminum-bearing. However, their aluminum content is either lower than the aluminum content of the rock as a whole or, at most, of approximately equal magnitude.

According to Bowen and Greig (1924), aluminum forms two silicates at elevated temperatures in the system $\text{Al}_2\text{O}_3\text{-SiO}_2$, viz.,



The silicate $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, metakaolinite, is also known; it is obtained by removing water from kaolinite, $\text{Al}_4[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$. However, metakaolinite is not stable at elevated temperatures and cannot be obtained by direct crystallization from aluminum silicate melts. Both mullite and sillimanite occur as minerals; the compound $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ is found, in addition, as andalusite and kyanite. The optical properties of mullite and sillimanite are very nearly identical, and they cannot be distinguished from each other except by X-ray diffraction studies or chemical analysis. Mullite, however, is very rare; it is found only incidentally at igneous contacts. Sillimanite, andalusite, and kyanite, although rather common constituents of metamorphic rocks, are seldom found in igneous rocks and, when present, occur in small quantities at igneous contacts, as does mullite. Therefore, these silicates of aluminum are geochemically insignificant.

The foregoing discussion shows that aluminum is not present in igneous rocks as a simple silicate. It is always combined with other metals to form complex aluminosilicates. X-ray diffraction studies have revealed two entirely different manners of occurrence of aluminum in silicate minerals.

All silicate minerals consist of a framework of $[\text{SiO}_4]$ tetrahedra, which are combined in various ways in the different mineral groups and form regular structures. In the $[\text{SiO}_4]$ tetrahedra, a part of Si^{4+} may be replaced by Al^{3+} . Owing to the great difference between the sizes of these ions, their radii being 0.39 and 0.57 kX, respectively, the substitution is never complete. Its degree depends, in addition, on the structural type of the mineral in question. In the feldspars all aluminum present replaces silicon in the Si-O tetrahedra, and only the ions K^+ , Na^+ , Ca^{2+} , etc., form the cation network. In like manner, Al^{3+} partly replaces Si^{4+} in the amphiboles, pyroxenes, and micas. In the amphiboles, only one-third of the Si^{4+} ions may be re-

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placed by Al^{3+} . In these minerals aluminum is also found outside the silicon-oxygen framework, occupying a position similar to that held by Mg^{2+} and Fe^{2+} . In spite of its somewhat smaller size, aluminum in this case replaces Mg^{2+} (radius 0.78 kX) and Fe^{2+} (radius 0.83 kX) diadochically. It occurs, like these ions, between the oxygen ions located in the corners of the $[\text{SiO}_4]$ tetrahedra. The co-ordination number of aluminum is usually 6. The Fe^{3+} ions have a similar manner of occurrence. In other important groups of silicate minerals aluminum also occupies two different structural positions.

Aluminum, like calcium and magnesium, usually does not occur in igneous rocks as a simple oxide. Corundum, $\alpha\text{-Al}_2\text{O}_3$, is present only when aluminum predominates over both calcium and the alkali metals; if such is the case, all aluminum cannot be bound in the feldspars. The presence of corundum in pegmatites, metamorphic rocks, etc., is therefore a proof of an exceptionally high content of aluminum.

Other aluminum minerals include chrysoberyl, Al_2BeO_4 , found in granite pegmatite, aplite, and mica schist; topaz, $\text{Al}_2[\text{F}_2|\text{SiO}_4]$, which is connected with pneumatolytic activity; many halogenides, e.g., fluellite, $\text{AlF}_3 \cdot \text{H}_2\text{O}$; carbonates; and numerous phosphates and sulfates. However, all these minerals are geochemically rather unimportant.

CYCLE OF ALUMINUM

The cycle of aluminum is simple, and its details are well known. During the weathering, the feldspars and some other silicates, for example, leucite, go into ionic solution. Under normal conditions these minerals are completely dissolved, at least in the beginning of the weathering. Aluminum remains dissolved both in acid solution with pH less than 4 and in basic solution ($\text{pH} > 9$); and aluminum hydroxide, $\text{Al}(\text{OH})_3$, is precipitated only in the neighborhood of the neutral point. Aluminum hydroxide is also precipitated when the solution becomes concentrated because of evaporation. If an acid solution turns neutral or alkaline—e.g., because of the escape of carbon dioxide, the main agent causing acidity in natural waters, or by reaction with calcium carbonate—aluminum hydroxide is precipitated. Because silica remains in solution under these circumstances, aluminum deposits of a considerable degree of purity may thus be formed. However, alumina and silica may also react with each other to form crystalline clay minerals, and a small part of the two compounds may coagulate as hydrogels. It is known that silica and alu-

mina sols of a concentration of approximately 0.1 per cent quickly precipitate each other. During the weathering of the micas the disintegration is often incomplete, and chiefly the alkali metals are extracted. The silicon-oxygen framework thus remains largely unattacked and may be easily converted, in reactions with the weathering solutions, into clay minerals.

The clay minerals are hydrous aluminum silicates. Some aluminum is often replaced by Fe^{3+} and Mg^{2+} and by small amounts of alkali metals and alkaline-earth metals. The most important clay minerals are illite, similar in composition to the white micas, although not identical therewith; montmorillonite, $\text{Al}_2[(\text{OH})_2|\text{Si}_4\text{O}_{10}]\cdot n\text{H}_2\text{O}$; and kaolinite, $\text{Al}_4[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$. Illite contains potassium as an essential constituent.

Geochemically important is the base-exchange capacity of the clay minerals, particularly of montmorillonite, which is partly caused by structural substitution. The alkali metals are rather readily replaced, whereas the alkaline-earth metals are more tightly held in the structure.

According to Noll (1936), whether montmorillonite or kaolinite will be formed during the weathering depends on the amount of alkali metals and alkaline-earth metals removed during the decomposition and on the pH of the weathering solutions. When the above-mentioned metals are thoroughly removed by circulating waters and when the solution is acid or much carbon dioxide is present, kaolinite is predominantly formed. On the other hand, montmorillonite is formed if the leaching is incomplete and the solution is alkaline or neutral. Noll (1935) considers the formation of montmorillonite possible in sea water, whereas in river and bog water the formation only of kaolinite will take place. Also, if iron is leached out during the weathering, e.g., as ferrous compounds stable in the presence of carbon dioxide, sulfuric acid, and humic substances, the kaolinite will be quite pure. Such deposits are of importance as raw materials for the ceramic industry.

Kaolinitic clay minerals are normally produced during podzolization in forest soil in temperate and humid climates. On the other hand, the clay minerals are often decomposed, with a consequent leaching of silica, when tropical weathering takes place. Aluminum hydroxide, along with ferric hydroxide, is widely distributed among the products of tropical weathering, but it is known also in some limestone soils (terra rossa) of Mediterranean climates.

All clay minerals have phyllosilicate structures, with Al^{3+} as the most important and most common cation. Like the micas, the clay minerals contain the $[\text{SiO}_4]$ tetrahedra arranged in the form of two-dimensional sheets, which, however, are not directly linked by cations to form three-dimensional networks. Most clay minerals contain a separate $\text{Al}(\text{O},\text{OH})_6$ sheet intercalated between two sheets of $[\text{SiO}_4]$ tetrahedra. In the micas the cation (Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , etc.) and the Si^{4+} ion share an oxygen ion, whereas in the clay minerals there are either two oxygen ions, $-\text{O}-\text{O}-$, or an oxygen and a hydroxyl, $-\text{O}-\text{OH}-$, between the silicon and the aluminum ions. In the groups $\text{Si}-\text{O}-\text{O}-\text{Al}$ and $\text{Si}-\text{O}-\text{OH}-\text{Al}$ the bond between Si and Al is weaker than the corresponding bond in the group $\text{Si}-\text{O}-\text{Al}$ of the micas. In the clay minerals, which are always formed at low temperatures, aluminum seems almost completely unable to replace silicon diadochically in the $[\text{SiO}_4]$ tetrahedra. At any rate, this replacement is much more limited than in the aluminosilicates of igneous rocks. In clay minerals, aluminum is nearly always found outside the silicon-oxygen framework as a cation with a co-ordination number 6, and thus the manner of occurrence of aluminum in clay minerals differs notably from that in the aluminosilicates of igneous rocks.

One of the effects of the difference between the crystal structure of the micas and the clay minerals is that in the latter the cleavage parallel to the sheets in the structure is often more prominent than in the former minerals. The perfect cleavage causes the formation of very finely divided particles during the transportation. During the settling in the sea the clay minerals and the chemically unaltered, but equally finely divided, mineral grains, consequently, become separated from the coarser-grained resistates, and clays of high purity may be formed which are valuable as raw materials for the ceramic industry.

The enrichment of aluminum in the hydrolyzates is a feature most characteristic of this group of sediments. Although the average aluminum content of igneous rocks (8.13 per cent) given in Table 2.3 is nearly equal with the corresponding average for Norwegian clays (8.37 per cent), calculated from the value presented by Goldschmidt (1933a), the fact must be taken into account that these clays are glacial clays, deposited in a cold climate and therefore showing only relatively small chemical changes. In clays formed during intensive weathering the chemical changes are more pronounced, and consequently their aluminum content is usually higher. Although the con-

tent of aluminum in river water is low, this metal is constantly present therein. Table 6.17 shows that the aluminum content of sea water is very low. The geochemical balance of aluminum in sea water (Table 6.19) also shows that the transfer percentage in this case is extremely low. These observations show that aluminum does not remain permanently in the solutions produced during the weathering. Its hydroxide is weakly basic, and therefore the soluble aluminum salts, in common natural waters, are promptly hydrolyzed and subsequently removed in the solid products of weathering. Therefore, the residates become impoverished in aluminum, whereas the hydrolyzates become enriched therein, and it is evident that the content of aluminum in the hydrolyzates will increase parallel to the degree of change in their chemical composition. The deposition of aluminum in the hydrolyzates is almost quantitative, i.e., the quantity of aluminum liberated from the minerals during their weathering is quantitatively transported into the hydrolyzates, and only very little is found in precipitates, oxidates, evaporates, and sea water.

After their deposition the hydrolyzates are aged long before the diagenetic processes commence their work. The aging consists of the crystallization of the still remaining gels to form clay minerals. The indurated sediments may participate in metamorphic phenomena, during which mica schists and other rocks with a chemical composition corresponding to that of the original argillaceous sediments may be formed. All such rocks are characterized by a high content of aluminum, which may serve as a criterion indicating whether a strongly metamorphosed rock is of igneous or of sedimentary origin.

ALUMINUM IN THE BIOSPHERE

Aluminum is widely distributed in all organisms, but it is believed to be a relatively unimportant constituent in them. This belief is due to the low solubility of the compounds of Al^{3+} in neutral solution (Hutchinson, 1945). However, aluminum might be essential for higher plants. Plants contain considerably more aluminum than animals do, and some plants are known to accumulate this metal. The most remarkable case is that of a tree, *Orites excelsa*, in which a basic aluminum succinate is reported to occur in trunk cavities. *Lycopodium alpinum* may contain 33 per cent Al_2O_3 in its ashes. In these plants, however, aluminum is a typical ballast element. It is also somewhat concentrated in coal ashes. Aluminum salts of organic acids also occur elsewhere in the biosphere, e.g., $\text{Al}_2[\text{C}_{12}\text{O}_{12}] \cdot 18\text{H}_2\text{O}$, found, as mel-

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lite, in brown coal. Many plants are very sensitive to aluminum, because the Al^{3+} ions are pronounced precipitants of negatively charged colloids. This property of aluminum may thus have important effects on the properties of cultivated soil.

Lower animals are usually higher in aluminum than are higher ones. There is some evidence that aluminum is involved in the oxidation of succinates in the mammals. Some other trivalent elements (Cr, Nd, La, Sm) may substitute for aluminum in this process.

Diatoms are known to be able to decompose clay minerals, thus causing biological liberation of aluminum compounds.

ALUMINUM ORES

A number of large aluminum-ore bodies are pure weathering products located *in situ*. The most important aluminum ores consist of bauxite and are the result of lateritic weathering. Bauxite and laterite consist of diaspore, $\alpha\text{-AlOOH}$; boehmite, $\gamma\text{-AlOOH}$; gibbsite (hydrargillite), $\gamma\text{-Al(OH)}_3$; ferric hydroxide, etc. With the exception of cryolite, all aluminum ores of technical importance are of sedimentary continental origin. The bauxite deposits are often located in their original place, and it is consequently possible to account for the nature of the parental rock. There are siliceous and calcareous bauxites, which are chemically rather similar. The siliceous bauxites are formed during a prolonged lateritization of igneous rocks, preferably of basic ones, e.g., gabbros, diabases, and, particularly, basalts. Carbonated ground waters may play an active part in the direct formation of aluminum hydroxide from basic igneous rocks. This group includes, for example, bauxites in Germany, those in the French Central Plateau, and the Arkansas deposits in the United States. Many of these deposits are found in areas showing evidence of Tertiary volcanic activity. They afford proof of the existence of a tropical climate during their formation. The calcareous bauxites are formed from impure argillaceous limestones under the action of carbon dioxide-bearing waters in a warm climate. The clayey material in the limestone is converted into bauxite, and the calcium carbonate is removed as bicarbonate. Such bauxite deposits are common in many places in central, eastern, and southern Europe, e.g., in southern France and at Tikhvin, south of Lake Ladoga in the U.S.S.R.

Kaolin, a mixture of kaolinite and other clay minerals, both crystalline and amorphous, is an important raw material of the ceramic industry.

Compared with bauxite, all other aluminum ores used are of relatively small importance. Cryolite, $\text{Na}_3[\text{AlF}_6]$, is mined at Ivigtut in western Greenland. This deposit is the only one of economic importance. The cryolite forms a huge intrusive body in granite and was evidently formed at a rather low temperature. The cryolite body is next comparable to the minerals ofmiarolitic cavities often found in granites. The cryolite used as a flux in metallurgical processes is mostly artificial.

Some silicate minerals rich in aluminum have recently been introduced as aluminum ores. At Boliden, Sweden, andalusite, $\text{Al}_2[\text{O}|\text{SiO}_4]$, was mined for this purpose. The ore consists of andalusite rock formed by replacement of acidic to intermediate volcanic rocks.

THE RARE-EARTH METALS: SCANDIUM, YTTRIUM, THE LANTHANIDES

THE GROUP OF THE RARE-EARTH¹ METALS

IN THIS book the group called the rare-earth metals includes scandium ($Z = 21$), yttrium ($Z = 39$), and the lanthanides from lanthanum ($Z = 57$) to lutetium (cassiopeium; $Z = 71$). Often only yttrium and the lanthanides are classified as rare-earth elements proper, and also other groupings are presented, all of which show that the term rare-earth elements is somewhat indefinite. Yttrium is here included because it is very closely associated with the lanthanides in Nature and resembles them chemically in many respects. Scandium is included because of its close chemical relationship to yttrium.

On account of its chemical properties, thorium also is often included in the group of the rare-earth metals. It resembles scandium chemically in many respects. However, even though its manner of occurrence rather closely resembles that of the rare-earth metals, it differs geochemically from them in many points and consequently is not discussed in this chapter. Moreover, it is now known that thorium forms with actinium, protactinium, uranium, and the transuranium elements a series of elements which are called thorides when quadrivalent and actinides when trivalent (Zachariasen, 1948). The thorides and the actinides resemble the lanthanides in many respects.

It was pointed out in chapter 5 that the lanthanides form a notable exception to the general regularity in the Periodic System. The addition of new f -type electrons to the atom when the proton number increases will take place prematurely in the inner N shell, whereas the outer shells remain unchanged. The result is a $4f$ series of elements which are chemically very similar to one another and, consequently,

1. The name earth (German *Erde*) originally referred to any not readily reducible oxides of metals. They were formerly believed to be elements. The alkaline earths include the oxides of calcium, strontium, and barium. The earth acids are the oxides of columbium and tantalum. *Tonerde* is alumina.

show notable similarities in their geochemical behavior. The decrease in the size of the ionic radius in the lanthanide series, called the lanthanide contraction (see chap. 5), is also explained by these peculiarities in the atomic structure. Owing to the analogy in the structure of their electron shells, scandium and yttrium also rather closely resemble the lanthanides chemically. Scandium, however, differs from the lanthanides geochemically in certain essential points—a difference caused by its decidedly smaller ionic size.

The samarium isotope Sm^{152} is radioactive and is the only known α -ray emitter found in Nature, with the exception of the members of the three heavy radioactive series. However, because of the low abundance of samarium and the scarcity of Sm^{152} , the amount of helium contributed by samarium is negligible, compared with the quantity produced by other radioactive elements (Evans and Goodman, 1944).

The half-life of Sm^{152} is $1.0 \cdot 10^{12}$ years. Another long-lived naturally radioactive isotope is the rare Lu^{176} , with a half-life of $2.4 \cdot 10^{10}$ years. Its radiation consists of γ -rays and negative β -particles.

ABUNDANCE AND GEOCHEMICAL CHARACTER OF THE RARE-EARTH METALS

The rare-earth metals, the lanthanides in particular, form a geochemically rather coherent group. It is believed that they accordingly still display the original abundance relationships which have suffered few, if any, changes because of physical and chemical processes causing selective separation.

The abundance of the rare-earth metals in silicate meteorites and in the upper lithosphere is presented in Table 18.1. In addition, the atomic abundances of the lanthanides, referred to $Y = 100$, are presented in Figure 18.1, which is taken from Goldschmidt (1937*a*). The observations of Goldschmidt and Thomassen (1924) on lanthanide minerals, Russell (1929) on the solar atmosphere, Minami (1935*a*) on shales, and Noddack (1935) on stony meteorites form the basis of this figure. Goldschmidt (1937*b*) has expressed the belief that the lower abundance of cerium with respect to neodymium in silicate meteorites is probably due to an analytical error.

Contrary to what is the case with most other elements, the average abundance of the rare-earth metals in the upper lithosphere has not been determined in igneous rocks but in argillaceous sediments. Such practice is legitimate, provided that no appreciable quantities of the

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elements in question are found in volcanic emanations and that the amount finally remaining in the sea during the processes of weathering and the formation of sediments tends to be very small.

Actually, the name rare-earth metals, which was first applied to the members of this group of elements, is no longer consistent with their real abundance. The values presented in Table 2.3 make evident that these elements are, in fact, not rare but considerably more abun-

TABLE 18.1
ABUNDANCE OF THE RARE-EARTH METALS

MATERIAL	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu
	g/ton								
Silicate meteorites (Noddack, 1935) . . .	5 80	6 13	2 05	2 30	0.97	3 37		1 23	0 30
Silicate meteorites (Goldschmidt, 1937b)	5								
Shales (Minami, 1935a)		28.1	18 3	46.1	5 53	23 9		6.47	1 06
Upper lithosphere (Goldschmidt, 1937b)	5								
Igneous rocks, Dutch East Indies (van Tongeren, 1938). . . .	2 7	17.4	19 6	24 7		18 1			

MATERIAL	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	g/ton							
Silicate meteorites (Noddack, 1935) . . .	1.84	0.58	2.34	0 66	1 93	0 34	1 85	0.60
Shales (Minami, 1935a)	6 36	0 91	4 47	1 15	2.47	0.20	2 66	0.75

dant than many metals of technical importance, not necessarily considered rare in everyday life.

Scandium, yttrium, and the lanthanides are present in the Sun's atmosphere, however, with the exception of terbium, which has not been detected with certainty, and holmium, the presence of which is unsettled. All these elements are present in very low concentrations in the metal and sulfide phases of the meteorites. In the silicate phase the abundance of scandium is as high as in the upper lithosphere, whereas the abundance of yttrium and the lanthanides is from two to ten times lower in the silicate meteorites than in the upper lithosphere.

The lanthanides form a convincing example of the validity of the rule of Oddo and Harkins. Figure 18.1 gives conclusive evidence of the fact that the lanthanides with odd atomic number are, as a rule, less abundant than their even-numbered neighbors, both in cosmic and in terrestrial surroundings.

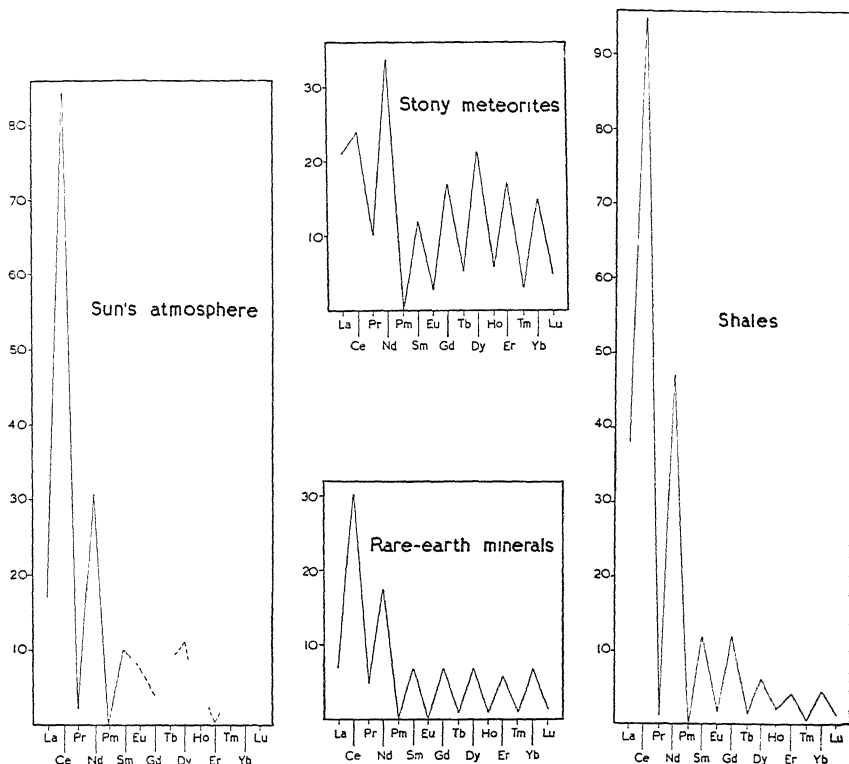


FIG. 18.1.—The atomic abundance of the lanthanides in the solar atmosphere, stony meteorites, lanthanide minerals, and shales.

The rare-earth metals are all strongly lithophile. Their lithophile character increases with increasing ionic radius. In the series Sc-Y-La the basic properties of the hydroxides increase toward lanthanum, the oxides grow less readily reducible, and the lithophile behavior of the elements increases. In the upper lithosphere all rare-earth elements are strongly oxyphile.

SCANDIUM IN IGNEOUS ROCKS

Scandium was previously considered one of the rarest elements because its presence was established in very few minerals and, besides,

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it occurred therein only as a temporary constituent and in negligible amounts. However, Meyer (1908) found a notable content of scandium in wolframite, and Eberhard (1908, 1910) proved that scandium is a common and relatively abundant metal which may be detected by spectrochemical analysis in numerous rocks and minerals. Eberhard found the highest scandium content in minerals of granites and granite pegmatites, such as cassiterite, wolframite, euxenite, monazite, eschynite, keilhauite, and zinnwaldite. Vernadsky (1924), using Eberhard's results, considered scandium a typically dispersed element, which is evenly distributed in small quantities among various rocks. In addition, Vernadsky remarked that the minerals richest in scandium usually are typical of granites and their pegmatites.

Goldschmidt and Peters (1931*b*) found that the bulk of the scandium present in the upper lithosphere is concealed in the ferromagnesium minerals of the early crystallates and of ultrabasic and basic rocks, such as pyroxenites and gabbros. Goldschmidt (1939) reports a maximum content of 116 g/ton Sc in pyroxenite. Scandium also occurs in the ferromagnesium minerals of silicic rocks. The scandium content in the ferromagnesium minerals is usually of the order of 5–30 g/ton Sc.

According to Oftedal (1943), practically all the scandium in igneous rocks is contained in pyroxenes, amphiboles, and biotite. He found a maximum content of 150 g/ton Sc in pyroxenes of basic igneous rocks and 200 g/ton Sc in the hornblende of a hornblende gabbro. The content in biotite and muscovite of granite pegmatites was up to 1,000 g/ton Sc and in beryl as high as 1 per cent. In silicic rocks the amphiboles probably tend to be lower in scandium than in basic rocks. The biotites are generally poor in scandium. According to Oftedal, biotite may be used as a geological thermometer, provided that it is the only ferromagnesium constituent of an igneous rock. The reason is that, when formed, the structure of biotite in many cases is saturated with scandium. Provided that none of this element is lost from biotite, a content of about 5 g/ton Sc in this mineral is a token of a high temperature of formation (basic and intermediate igneous rocks). A content of approximately 10–30 g/ton Sc indicates a low temperature of formation (acidic igneous rocks). The scandium content in metamorphic rocks is about 20 g/ton Sc. Biotites formed from granitic magmas and their residual liquors during the final magmatic stage contain 10–1,000 g/ton Sc. During the pneumatolytic-hydrothermal stage, scandium may still become enriched in the

early-crystallized micas, which are comparatively rich in iron. Thus Oftedal found 2,000 g/ton Sc in zinnwaldite from a granite pegmatite. During further decrease of temperature, scandium is not enriched in micas because it is no longer present. In beryl, scandium shows a behavior similar to that in micas.

The size of Sc^{3+} (radius 0.83 kX) permits its capture by Mg^{2+} (radius 0.78 kX) and Fe^{2+} (radius 0.83 kX) in mineral structures, but diadochically it cannot extensively replace Ca^{2+} (radius 1.06 kX), Al^{3+} (radius 0.57 kX), or Fe^{3+} (radius 0.67 kX). According to Wickman (1943), the E -value of Sc^{3+} must be high. Thus Sc^{3+} is unable to replace Mg^{2+} directly in all minerals, because Pauling's rules must be satisfied. This involves, among other things, the impossibility of a substitution of MgSi by ScAl in olivine.

The independent calcium and aluminum minerals of igneous rocks, such as plagioclase, nepheline, corundum, and the calcium-bearing garnets, usually contain little scandium or none at all. The reason for this lack is the difference in the size of ionic radii referred to above. In aluminum minerals, Sc^{3+} may replace Al^{3+} only provided that Al^{3+} is also replaced by Mg^{2+} or Fe^{2+} , e.g., in allanite.

Among the early crystallates the magmatic iron ores either are very low in scandium or contain none at all. In eclogites the garnet sometimes may contain a little more scandium than the pyroxene; the content runs as high as 65 g/ton Sc in both minerals (Goldschmidt and Peters, 1931b).

The part of scandium which is not seized during the main stage of crystallization by the rock-making minerals mentioned above remains in the residual liquors and becomes enriched in plumasitic pegmatites and pneumatolytic rocks; in particular, in many minerals of the cassiterite-wolframite paragenesis. Also in this case scandium preferentially occurs in minerals of the Mg^{2+} - Fe^{2+} - Mn^{2+} group, especially in wolframite. Many minerals of the plumasitic complex pegmatites are, consequently, relatively rich in scandium, but the agpaitic pegmatites do not carry this metal in important concentrations. Among the minerals of granite pegmatites, spessartite and tourmaline contain up to 65 g/ton Sc (Goldschmidt and Peters, 1931b), and still higher contents may be present in beryl (see above). Newhouse (1941) established the presence of scandium in magnetites associated with granite pegmatites. Wiikite, which is found in some granite pegmatites in eastern Fennoscandia (Impilahti), may contain in excess of 1 per cent Sc_2O_3 , according to the analysis made by Sir

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William Crookes in 1908. The only independent scandium mineral so far known is thortveitite, $\text{Sc}_2[\text{Si}_2\text{O}_7]$, which occurs in pegmatites of southern Norway and Madagascar and contains 41–42 per cent Sc_2O_3 . It is often quoted as a typical example of structures containing $[\text{Si}_2\text{O}_7]$ groups. Bazzite is reportedly another scandium silicate, which also contains other rare-earth metals, sodium, and iron.

Goldschmidt (1934, 1937*c*) found that the thortveitite at Ljosland in Norway has not received scandium from granitic residual solutions but from the surrounding ortho-amphibolite penetrated by the pegmatite veins. The amphibolite contains, on an average, 20 g/ton Sc, and the scandium has been leached out from the amphibolite into the pegmatite to form thortveitite.

Eberhard (1910) noticed a distinct, although usually weak, enrichment of scandium during pneumatolytic processes. In pneumatolytic plumasitic rocks, scandium is concentrated, particularly in cassiterite and wolframite. In both minerals the scandium content may be several tenths of 1 per cent. Goldschmidt and Peters (1931*b*) explained the presence of scandium in wolframite as a result of the isomorphism between $\text{Fe}^{2+}\text{WO}_4$ and $\text{Mn}^{2+}\text{WO}_4$, on the one hand, and ScCbO_4 and ScTaO_4 , on the other hand. Bivalent iron and manganese are replaced by trivalent scandium, and the substitution of the binegative $[\text{WO}_4]$ group by trinegative $[\text{CbO}_4]$ or $[\text{TaO}_4]$ maintains the electrical neutrality of the structure. It is a well-established fact that the wolframites frequently carry noteworthy amounts of columbium and tantalum (see chap. 26). In like manner, Sc^{3+} replaces Fe^{2+} in triplite, and the electrical neutrality of the structure is maintained by the substitution of quadrinegative $[\text{SiO}_4]$ for trinegative $[\text{PO}_4]$. Goldschmidt and Peters (1931*b*) report up to 325 g/ton Sc in triplite.

On the other hand, scandium does not replace calcium in scheelite. Its manner of occurrence in cassiterite is still unknown. Even though both columbium and tantalum are common constituents of cassiterite, the presence of ScCbO_4 and ScTaO_4 in the cassiterite structure is, so far, uncertain. If both wolframite and cassiterite are contemporaneously present, scandium is predominantly enriched in wolframite.

In rocks of hydrothermal and metasomatic origin, scandium also replaces bivalent iron and magnesium. Minute amounts of scandium are found in siderite, FeCO_3 , which contains, according to Goldschmidt and Peters (1931*b*), about 3 g/ton Sc. The reason is, according to Goldschmidt and Hauptmann (1932), that scandium orthoborate, ScBO_3 , which has a structure (of calcite type) and structural

dimensions similar to those of ferrous carbonate, forms isomorphic mixtures with the latter. A corresponding isomorphism exists between indium borate and calcium carbonate (see chap. 40). The general rule is that borates of such trivalent metals as have ionic radii similar to the radii of Mg^{2+} , Fe^{2+} , Mn^{2+} , and Zn^{2+} belong to the calcite type (In^{3+} , Sc^{3+} , Lu^{3+}), whereas borates of metals with ionic radii intermediate between the radii of Ca^{2+} and Sr^{2+} in size belong to the aragonite type (La^{3+} , Ce^{3+} , Pr^{3+}).

The manner of occurrence of scandium in the silicate minerals of magnesium is unknown. Goldschmidt and Peters (1931*b*) suggested that B-O complexes might substitute for Si-O complexes when magnesium is replaced by scandium. They found 6.5 g/ton Sc in serpentine and chlorite of a probable igneous origin. The results of Sahama (1945*b*) seem to afford proof of this assumption, because he found a substantial content of boron in serpentinites (see chap. 16).

The radius of Sc^{3+} is considerably smaller than the radii of La^{3+} (1.22 kX) and of the trivalent lanthanides, and therefore scandium does not constantly accompany these metals in minerals. If scandium occurs together with considerable amounts of the lanthanides, only such members of the lanthanide series are especially concentrated as have the smallest ionic radii of all, i.e., ytterbium and lutecium, which actually occur in thortveitite. An example of the Sc^{3+} - In^{3+} assemblage, the existence of which Goldschmidt and Peters (1931*b*) considered possible, seems to be the pegmatite investigated by Romeyn (1933), which contains 1.0–2.8 per cent In and 0.5–1.2 per cent Sc. The zirconium minerals contain only small quantities of scandium or are totally devoid of it because Sc^{3+} , notwithstanding the similarity of the ionic radii, cannot substitute for Zr^{4+} , owing to its unusually low concentration. Thortveitite, however, contains notable amounts of zirconium and hafnium, which replace scandium in the structure. The electrical balance is maintained by the substitution of Si^{4+} by Be^{2+} in the silicon-oxygen complexes.

The content of scandium in igneous rocks is illustrated by the analyses presented in Table 18.2. The enrichment of scandium in basic rocks is once more established by the analyses. This enrichment and the concentration of scandium in ferromagnesium minerals in general show that scandium cannot be a dispersed element in the sense advocated by Vernadsky (1924). Another conclusion based on Table 18.2 is that scandium does not follow aluminum during the differentiation.

CYCLE OF SCANDIUM

The discussion in the preceding paragraph shows that, even though scandium chemically resembles yttrium and the lanthanides to a considerable extent, it differs materially from them in its manner of occurrence in igneous surroundings. Corresponding differences are also found in phenomena related to weathering and the formation of sediments; evidently, these differences are due to the smaller ionic size and weaker basic properties of scandium as compared with yttrium and the lanthanides. In accordance with the greater radius of Sc^{3+} , scandium hydroxide is somewhat more basic than is aluminum hydroxide. On the other hand, the radius of tripositive scandium

TABLE 18.2
CONTENT OF SCANDIUM IN IGNEOUS ROCKS

Rock	Sc (g/ton)	Sc ₂ O ₃	MgO	Al ₂ O ₃
		Per Cent		
Pyroxenites (Goldschmidt, 1934, 1937c)	46	0 007	20	5
Gabbros (Goldschmidt, 1934, 1937c)	20	0 003	8	18
Basalts (Goldschmidt, 1934, 1937c)	6 5	0 001	6	16
Andesites (Goldschmidt, 1934, 1937c)	4 6	0 0007	3	17
Granites (Goldschmidt, 1934, 1937c)	1 3	0 0002	1	15
Nepheline syenites (Goldschmidt, 1934, 1937c)	0	0	1	20
Ultrabasics, southern Lapland (Sahama, 1945b)	6 5	0 001		
Gabbros and dolerites, southern Lapland (Sahama, 1945b)	20	0 003		
Granites, southern Lapland (Sahama, 1945b)	0 7	0 0001		
Syenites, southern Lapland (Sahama, 1945b)	2	0 0003		

is smaller than the radius of tripositive yttrium and lanthanum, and therefore scandium hydroxide is less basic than yttrium hydroxide and lanthanum hydroxide. In iron-bearing hydrolyzates and oxides, such as the red clay, the Sc:Al ratio is nearly equal to the average ratio in the upper lithosphere. Such hydrolyzate sediments, however, which have lost the metals that form hydroxides more basic than aluminum hydroxide, contain but little scandium. Thus scandium has been leached out during the formation of bauxite. Because $\text{Sc}(\text{OH})_3$ is more readily soluble than $\text{Al}(\text{OH})_3$, scandium tends to become enriched in oxidate sediments, for example, in sedimentary iron ores. However, no enrichment of scandium seems to take place in manganese ores of sedimentary origin. In carbonate sediments the content of scandium is negligible, and in this respect the behavior of scandium is just the reverse of the behavior of yttrium and the lan-

thanides. The content of scandium in sea water is very low, and the low value of the transfer percentage (see Table 6.19) shows that scandium is nearly quantitatively removed from sea water in the bottom sediments. For the same reason scandium is practically absent in the evaporates.

Table 18.3 shows the content of scandium in some sediments and their derivatives. Unfortunately, the number of analyses available is still far from sufficient.

Practically nothing is known about the migration of scandium during metamorphism. Eberhard (1908) found that, in a garnetiferous

TABLE 18.3
CONTENT OF SCANDIUM IN SEDIMENTS AND THEIR DERIVATIVES

Material	Sc (g/ton)
Bauxite, average (Goldschmidt and Peters, 1931b)	2
Terrigenous mud (Goldschmidt and Peters, 1931b) . . .	3
Glauconitic sandstone (Goldschmidt and Peters, 1931b)	3
Radiolarian ooze, <i>Globigerina</i> ooze (Goldschmidt and Peters, 1931b)	3
Red clay, average (Goldschmidt and Peters, 1931b) . . .	4.6
Manganese nodule (Goldschmidt and Peters, 1931b) . . .	3
Sedimentary iron ores (Goldschmidt and Peters, 1931b)	6.5-65
Quartzites, southern Lapland (Sahama, 1945b)	0.7
Aluminum-rich schists, southern Lapland (Sahama, 1945b)	6.5
Carbonate rocks, southern Lapland (Sahama, 1945b) . . .	0

mica schist, scandium was concentrated in garnet, whereas all the other minerals present in the rock were completely devoid of scandium. This observation would seem to mean that at least some migration of scandium might take place.

YTTRIUM AND THE LANTHANIDES

Yttrium and the lanthanides are typical examples of a group of elements the members of which constantly occur together in Nature. According to their chemical properties, these metals are divided into two subgroups, which are

Cerium-earth metals: La, Ce, Pr, Nd, (Pm), Sm, Eu

Yttrium-earth metals: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y

Other names used of these groups are the cerium group and the yttrium group. For brevity, they are often called cerium earths and yttrium earths. The abbreviation TR (French: *terres rares*) is sometimes used for these metals; it appears appropriate to designate the subgroups with TCe and TY. Europium is sometimes included in the

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yttrium group. Promethium, Pm, is an unstable radioactive element; it is discussed in chapter 46.

The compounds of the lanthanides are generally similar in both their physical and their chemical properties. The fluorides and oxalates are sparingly soluble. The basicity of the hydroxides varies: $\text{La}(\text{OH})_3$ is the most basic, and the basicity decreases with decreasing ionic radius when the valence remains constant.

According to the abundance values given in Table 18.1, the cerium-earth metals predominate in the upper lithosphere (shales), the most abundant among them being lanthanum, cerium, and neodymium. Yttrium is the most abundant yttrium-earth metal.

YTTRIUM AND THE LANTHANIDES IN IGNEOUS ROCKS

Eberhard (1908) emphasized the fact that lanthanum and yttrium are very common constituents of minerals and rocks, even though they occur in low concentrations; usually they occur along with scandium. However, owing to their larger ionic size, yttrium and the lanthanides cannot replace magnesium and ferrous iron in mineral structures. They become enriched in the residual liquors during the crystallization and are plentiful in granites and nepheline syenites. Sahama and Vähätalo (1939b) showed that yttrium and the lanthanides also become enriched in residual crystallates of basic rocks (diabase pegmatites). Yttrium and the lanthanides have a pronounced affinity for phosphorus and also for fluorine, which is displayed by numerous rare-earth minerals occurring in granite and nepheline syenite pegmatites. These minerals include yttrifluorite, $(\text{Ca}, \text{Y})\text{F}_{2-3}$; tysonite (fluocerite), LaF_3 ; the numerous multiple oxides which contain columbium, tantalum, titanium, uranium, and rare-earth metals, particularly yttrium (see Table 26.2), and which are characteristic of many complex granite and nepheline syenite pegmatites; coddazite (cerian ankerite), $(\text{Ca}, \text{Ce})(\text{Mg}, \text{Fe})[\text{CO}_3]_2$; the fluocarbonates bastnäsite, $(\text{La}, \text{Ce}, \dots)[\text{F}|\text{CO}_3]$, and parisite, $\text{Ca}(\text{La}, \text{Ce}, \dots)[\text{F}_2|(\text{CO}_3)_2]$; monazite, $\text{Ce}[\text{PO}_4]$, and xenotime, $\text{Y}[\text{PO}_4]$; thortveitite, $\text{Sc}_2[\text{Si}_2\text{O}_7]$; thalenite, $\text{Y}_2[\text{Si}_2\text{O}_7]$; gadolinite, $\text{Y}_2\text{Fe}[\text{O}|\text{BeSiO}_4]_2$; allanite (orthite), a rare-earth-bearing Fe-Ca-Al silicate which is a member of the epidote-zoisite group; rinkite, $\text{Na}(\text{Ca}, \text{Ce})_2(\text{Ti}, \text{Ce})[\text{F}|\text{SiO}_4]_2$; and some other titanium and zirconium silicates of calcium and the alkali metals. In addition, there is a number of other silicate and borosilicate minerals containing yttrium and the lanthanides.

Notable amounts of yttrium and the lanthanides may occur in zircon, $\text{Zr}[\text{SiO}_4]$, and thorite, $\text{Th}[\text{SiO}_4]$, which are isomorphic with xenotime. Mixed crystals are known: hagatalite and oyamalite, $(\text{Zr}, \text{Ce}, \text{Y})[(\text{Si}, \text{P})\text{O}_4]$, and auerlite, $(\text{Th}, \text{Ce}, \text{Y})[(\text{Si}, \text{P})\text{O}_4]$. Alvite is a zircon which contains hafnium, thorium, and the rare-earth metals.

Goldschmidt and Thomassen (1924) showed that, although the rare-earth metals form a geochemically strongly coherent group, their abundance in the above-mentioned minerals and in other independent rare-earth minerals varies considerably, owing to fractional crystallization and precipitation. Goldschmidt and Thomassen divided the rare-earth-bearing minerals into six types, which are characterized by the abundance graphs of Figure 18.2. The monazite and the allanite type are united in a single abundance diagram in this figure. The types are united, according to the degree of differentiation, into two main categories which are the complete and the selective assemblages. The complete assemblages contain all or nearly all lanthanides from lanthanum to lutecium, and there is no sharp difference between the abundance of the cerium-earth metals and that of the yttrium-earth metals. These assemblages are often found in minerals which contain rare-earth metals only as accessory constituents, e.g., in apatite and many gadolinites. In the selective assemblages, on the contrary, either the cerium earths or the yttrium earths predominate, as in allanite and xenotime. Consequently, the fractionation proceeds parallel to increasing or decreasing basicity in these assemblages.

The complete assemblages include two types: the apatite type and the yttrifluorite type.

In the apatite type the cerium earths predominate, and the mutual abundance relationships of the lanthanides are as follows:

$$\text{Ce} \geq \text{Nd} > \text{Sm} \geq \text{Gd} \geq \text{Dy} \geq \text{Er} \geq \text{Yb}.$$

In the yttrifluorite type, the yttrium earths are of the same abundance as the cerium earths, as in yttrifluorite, or they predominate. As in the apatite type, the even-numbered lanthanides from cerium to ytterbium are present, but the intermediate members and the ytterbium end of the series predominate. Therefore,

$$\text{Ce} = \text{Nd}, \text{ and often } \text{Nd} \sim \text{Sm} \sim \text{Gd}.$$

No marked peaks occur in the abundance graph.

The selective assemblages include types in which both cerium earths and yttrium earths may predominate. The monazite, thalen-

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ite, thortveitite, and xenotime types belong to these assemblages, as well as the wiikite type, established by Sahama and Vähätalo (1939a).

In the monazite type cerium earths predominate. This type is characterized by the metals from lanthanum to samarium, still with an appreciable content of gadolinium and often small amounts of other yttrium-earth metals. The mutual abundance relationships of the even-numbered elements are

$$\text{Ce} > \text{Nd} > \text{Sm} \geq \text{Gd}.$$

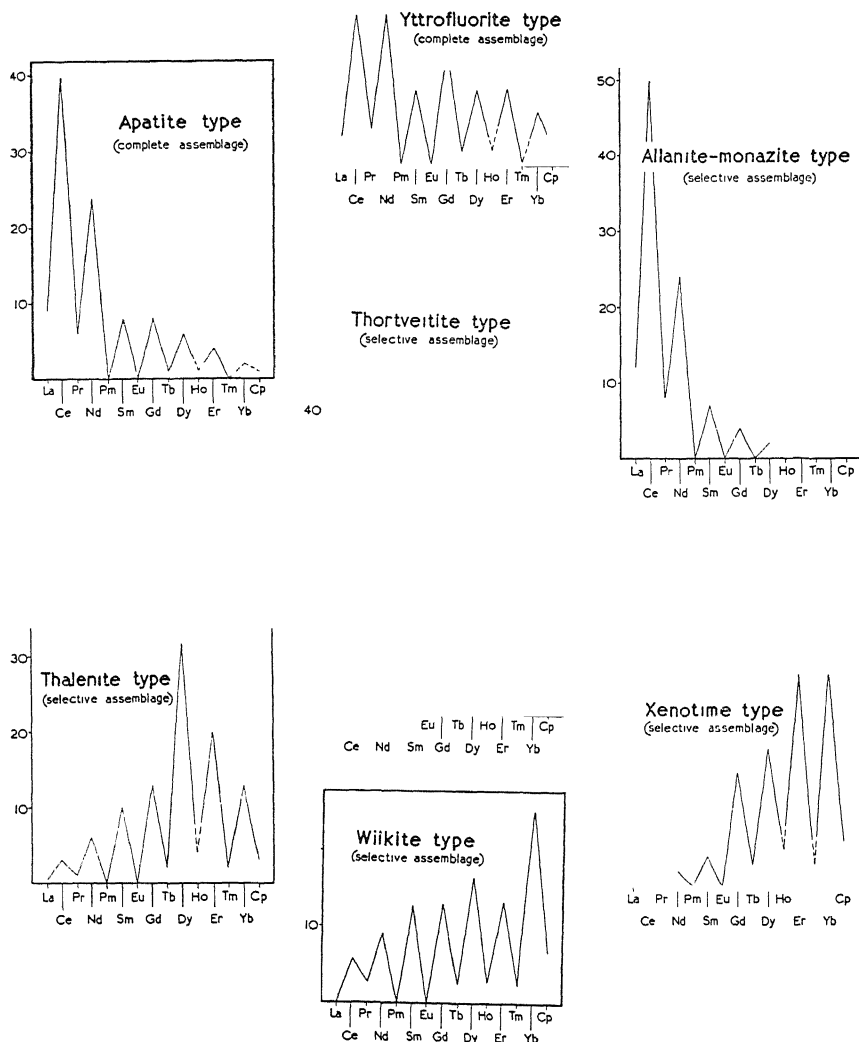


FIG. 18.2.—The seven types of the lanthanide composition of minerals

Monazite and fluocerite from granite pegmatites belong to this type. Intermediate types exist between the monazite type and the complete assemblages.

The allanite (orthite) type is characterized by the presence of the series La-Nd, small amounts of samarium and gadolinium, and sometimes traces of the other yttrium-earth metals. This variety includes, along with allanite, other cerium-earth silicates, among others, the lanthanum-rich minerals present in nepheline syenite pegmatites. The allanite type is the most pronounced cerium assemblage. The monazite type forms an intermediate between the complete assemblages and the allanite type. Compared with the apatite, the monazite and allanite types show that the series from samarium to ytterbium is impoverished.

The types with predominating yttrium earths have intermediates and all transitional types to the complete assemblages. In most yttrium-earth assemblages there still are notable amounts of the cerium earths present, and the effect of the progressive differentiation appears only in the shifting of a rather undecided maximum toward the higher atomic numbers, until ytterbium becomes the dominating lanthanide, as it is in thortveitite. The cerium end of the series may completely disappear during the change in the position of the maximum—xenotime is typical of this phase. The following four types belong to the selective assemblages with predominating yttrium-earth metals.

The thalenite type is characterized by a pronounced maximum at dysprosium and still with notable amounts of the cerium earths. It includes, along with thalenite, many gadolinites and a number of multiple oxides of columbium, tantalum, and titanium, and it still is not very far away from the complete assemblages.

The thortveitite type is characterized by a conspicuously high content of ytterbium and lutecium, along with much yttrium and scandium. The reason evidently is that the radii of Yb^{3+} (1.00 kX) and Lu^{3+} (0.99 kX) are closest to the radius of Sc^{3+} (0.83 kX). The rule is that when the lanthanides accompany scandium in minerals, a relatively high content of ytterbium and lutecium is always to be expected. In all minerals which have a lanthanide composition of the thortveitite type, i.e., in which ytterbium is strongly enriched, the yttrium-earth metals occur more or less as accessory constituents. It should be noticed, in addition, that hafnium is strongly enriched with respect to zirconium in thortveitite. Thortveitite is the foremost rep-

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representative of the thortveitite type, which is the rarest among the yttrium-earth assemblages.

The characteristic features of the xenotime type are the predominance of erbium and ytterbium, along with the presence of much gadolinium and dysprosium, and the strong impoverishment in all lanthanides preceding gadolinium. In this type, dysprosium, erbium, and ytterbium are rather uniformly distributed. The enrichment of the yttrium earths increases continually from the thalenite, through the thortveitite, to the xenotime type. The thortveitite and xenotime types are the most pronounced yttrium-earth varieties among the rare-earth assemblages.

The wiikite type is still another independent class among the selective assemblages. It was established by Sahama and Vähätalo (1939a), who found that its rare-earth composition was intermediate between the thalenite and the thortveitite types. The abundance graph of the wiikite type (calculated from wiikite No. 4437) is shown in Figure 18.2. Wiikite is chemically a rather complex multiple oxide of titanium, columbium, and tantalum with uranium and the rare-earth metals. It occurs only in the granite pegmatites at Impilahti in eastern Fennoscandia. In nearly all wiikites the yttrium earths, particularly yttrium, are in excess over the cerium earths, and a strong ytterbium maximum, along with a well-developed dysprosium submaximum, is present. In this respect wiikite shows a marked difference from the other columbium and tantalum minerals, investigated by Goldschmidt and Thomassen, in which dysprosium predominates but no ytterbium maximum is present. A comparison shows that more lanthanum and cerium is present in thortveitite than in wiikite.

The description of the types shows that only the first and the last metals in the lanthanide series may become enriched enough to predominate, viz., cerium (and lanthanum) in the allanite type and ytterbium (with lutecium) in the thortveitite type. This is a result of far-advanced chemical and crystal chemical fractionating processes. In like manner, only the end-members of the lanthanide series may become highly deficient and disappear altogether. In the center of the group the enrichment and impoverishment phenomena always incorporate several metals.

According to Goldschmidt and Thomassen (1924), the monazite type or the thalenite type might represent the original abundance distribution of the lanthanides. The calculation of the average composition of the assemblages (see Fig. 18.1) leads to a complete assem-

blage, in which the cerium-earth metals predominate. According to Goldschmidt and Thomassen, there is also petrological evidence which indicates that a complete assemblage with predominating cerium-earth metals closely corresponds to the original assemblage.

Haberlandt (1947) emphasizes the fact that the lanthanides become separated from one another, particularly the bivalent metals europium and ytterbium, perhaps also samarium. The rare-earth content of fluorite and feldspar depends on the manner of formation and the paragenetic relationships of these minerals. Thus bivalent europium is preferentially found in hydrothermal fluorites of ore deposits connected with intermediate igneous rocks, whereas bivalent ytterbium occurs in the low-temperature fluorites of granite pegmatites. The trivalent lanthanides become separated from one another in scheelite. Among the yttrium earths, terbium, dysprosium, and erbium are found chiefly in scheelites of granite pegmatites or otherwise related to residual granitic liquors, but europium and samarium usually occur in scheelites of ore bodies genetically connected with more basic igneous rocks. Also in sphene and in allanite the abundance of the lanthanides depends on the chemistry of the parent-rock. Sphenes rich in the yttrium earths are commonly found in granite pegmatites, but cerium-rich varieties of sphene occur in nepheline syenite pegmatites. Most allanites are enriched in cerium earths, but in some granite pegmatites the allanites may run relatively high in yttrium earths. According to Haberlandt, the cerium-earth metals, whose hydroxides are the more basic, are found in basic rocks, whereas the yttrium earths, which form less basic hydroxides, are concentrated in silicic igneous rocks. However, the lanthanide differentiation does not take place in all minerals: the cerium earths predominate in monazite and the yttrium earths in xenotime and zircon.

Most of the independent rare-earth minerals are constituents of granite and nepheline syenite pegmatites. In the minerals of the granite pegmatites the yttrium earths often predominate, whereas the bulk of the rare-earth metals found in minerals of nepheline syenites and nepheline syenite pegmatites usually consists of the cerium-earth metals. In accordance with their high redox potential, the nepheline syenites often contain considerable amounts of quadrivalent cerium along with trivalent cerium. However, most of the independent rare-earth minerals found in pegmatites are rare, geochemically speaking, and therefore they carry only a negligible part of yttrium and the lanthanides of the upper lithosphere. In conformity

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with scandium, the bulk of yttrium and the lanthanides is concealed in minerals formed during the main stage of crystallization. Only a relatively small part of these elements has become enriched in pegmatites.

Yttrium and the lanthanides, even when present in small quantities, show a notable tendency to form independent minerals in igneous rocks. Such minerals, e.g., allanite and monazite, which are common accessory constituents of many igneous rocks, are of high geochemical importance because they contain a very considerable part of the yttrium and lanthanides found in the upper lithosphere. Monazite, in addition, is the most important ore mineral of these metals. Another mineral of potential importance as a carrier of much of the supply of yttrium and the lanthanides is xenotime. Sahama and Vähätalo (1939*b*) emphasized the fact that xenotime occurs in many pegmatitic and muscovite-bearing granites and might thus be more common than previously held and might act as one of the carriers of the yttrium earths. Hutton (1947) established the common occurrence of monazite and xenotime as nuclei of pleochroic haloes in granites. This observation affords proof of the validity of the foregoing assumption.

Another part of yttrium and the lanthanides is incorporated in some other minerals which are not independent rare-earth minerals but contain these metals as nonessential constituents. Apatite, fluorite, sphene, zircon, garnet, and perhaps also biotite are the most important among such minerals. However, it must also be emphasized that there exists an yttrium-rich variety of sphene: keilhauite or yttrotitanite, $(\text{Ca}, \text{Y}, \text{Ce})(\text{Ti}, \text{Al}, \text{Fe}^{3+})[(\text{O}, \text{OH}, \text{F}) | \text{SiO}_4]$.

Apatite is the only common and quantitatively important mineral found in the early crystallates which contains notable amounts of yttrium and the lanthanides. The apatites of basic rocks (gabbro pegmatites) are richer in rare earths than are the apatites found in granite pegmatites and in pneumatolytic rocks. Britholite, $(\text{Na}, \text{Ce}, \text{Ca})_5[\text{F} | (\text{SiO}_4, \text{PO}_4)_3]$, a member of the apatite group, is found in nepheline syenites, and the Chibina apatites of the Kola Peninsula in Russia are of this composition. In like manner the sphenes of the Kola Peninsula are cerium-dominant (Sahama, 1946). Another rare-earth (yttrian) apatite is abukumalite, $(\text{Y}, \text{Th}, \text{Ca})_5[(\text{F}, \text{O}) | (\text{SiO}_4, \text{PO}_4, \text{AlO}_4)_3]$.

Fluorite, sphene, and garnet contain, in general, relatively more yttrium-earth metals than do allanite and monazite. They are, ac-

cordingly, carriers of a considerable proportion of the total of the yttrium earths. Apatite, monazite, and the minerals of the epidote-zoisite group, on the other hand, are important carriers of the cerium earths. Goldschmidt and Peters (1931*b*) showed that small amounts of yttrium, and evidently of the other yttrium-earth metals as well, are present in many early-crystallized calcium minerals, such as pyroxenes, amphiboles, and garnets. In all such minerals the yttrium-earth metals are captured to replace calcium. The yttrium-earth metals are concentrated because their ionic radii are closer to the radius of the bivalent calcium ion than are the radii of the cerium-earth metals. This also explains the concentration of the yttrium-earth metals in calcites of mineral veins and the relative enrichment of bivalent ytterbium, compared to the other yttrium-earth metals, in certain calcium minerals.

Because the anorthite component, $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$, of the plagioclase feldspars is the most common calcium compound found in igneous rocks, it might be suggested that a small part of calcium in plagioclase would be replaced by the rare-earth metals. However, according to Schiebold (1931), this is theoretically improbable. Plagioclases usually contain very small quantities of yttrium and the lanthanides. These metals, on the other hand, are found in potash feldspars, but the cerium earths always predominate there. The explanation is that the lanthanides replace potassium in the feldspar structure, and the similarity between the ionic radii is closer in the case of the cerium-earth metals than in the case of the yttrium-earth metals. Actually, the ionic radius of trivalent lanthanum is greater than the radii of the trivalent lanthanides, and this property leads to a partial separation of lanthanum from the lanthanides by its incorporation in the potash feldspars. Therefore, as pointed out by Goldschmidt (1937*b*), lanthanum might tend to follow an independent course during crystallization, but the separation is very much less complete than the separation of europium (see below).

Wickman (1943), in a discussion dealing with the behavior of the rare-earth metals during magmatic crystallization, pointed out that yttrium and the yttrium earths resemble bivalent calcium in co-ordination, whereas the cerium-earth metals prefer a somewhat higher co-ordination number. The E -values of the rare-earth metals are relatively high, and therefore these metals should occur in the early crystallates. However, they are usually concentrated in the residual liquors, and the reason is that it is not possible to maintain the elec-

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trical neutrality of the structures when the rare-earth metals substitute for the big cations in silicate minerals. In the pairs $\text{Sc}^{3+}\text{-Mg}^{2+}$, $\text{Ba}^{2+}\text{-K}^+$, $\text{Sr}^{2+}\text{-K}^+$, and $\text{Ca}^{2+}\text{-Na}^+$ it is commonly possible to replace Si^{4+} by Al^{3+} ; but, when the rare-earth metals are dealt with, the only possibility is the substitution of Si^{4+} by Be^{2+} in the silicon-oxygen tetrahedra. Because the E -value of Be^{2+} is low, beryllium is an element of the low-temperature assemblages, and yttrium and the lanthanides cannot be incorporated in the feldspar structure at elevated temperatures when beryllium is absent. According to Wickman, the trivalent lanthanides become enriched in beryllium-bearing feldspars. On the other hand, the bivalent europium ion may already enter the feldspars at high temperatures just as bivalent strontium does. Therefore, the early-formed alkali feldspars are able to concentrate europium.

In structures in which the electrical neutrality is maintained by ions with large E -values, yttrium and the lanthanides may become incorporated even at high temperatures. Yttrium may replace calcium in apatite, and the valence requirements are adjusted by substituting Si^{4+} for P^{5+} in the anion complex. In sphene it is possible to exchange Ti^{4+} for Fe^{3+} or Al^{3+} :



The explanation of the presence of yttrium in garnet is the resulting decrease in the charge of the 6-co-ordinated ions by one unit.

Even though the general laws that govern the manner of occurrence and distribution of yttrium and the lanthanides are known, the detailed information regarding their content in igneous rocks and minerals is rather incomplete. The content of yttrium in minerals is rather well known. Goldschmidt and Peters (1931*b*) report the following contents: ferromagnesium minerals (olivine, pyroxenes, amphiboles), 0–8 g/ton Y; garnets, zinnwaldite, wolframite, up to 8 g/ton; triplite, scheelite, nepheline, siderite, less than 8 g/ton; minerals of plumasitic pegmatites (corundum, beryl, tourmaline, micas), 0 g/ton; aegirite (from granite pegmatite), columbite, spessartite, 79–790 g/ton; eucolite, orangite, 790 g/ton. Sometimes the enrichment of yttrium in garnet is very considerable (yttrian almandite). Sahama (1936) found that yttrium (as well as scandium) was enriched in garnet and hypersthene in the granulites of Finnish Lapland; lanthanum, cerium, and europium were enriched in feldspars. Scandium was evenly distributed between garnet and hypersthene,

whereas the bulk of yttrium occurred in the garnet. Sahama reported the following maximum contents: in potash feldspar 425 g/ton La, 425 g/ton Ce, 4 g/ton Y; in garnet 470 g/ton Y.

The content of yttrium in the various classes of igneous rocks is presented in Table 18.4. According to Goldschmidt and Peters (1931*b*), yttrium is absent in magmatic iron ores. Goldschmidt, Hauptmann, and Peters (1933) found that yttrium is relatively strongly concentrated in acidic rocks.

According to van Tongeren (1938), the content of ytterbium in the igneous rocks of the Dutch East Indies is of the order of 0.9 g/ton Yb.

The analyses of Minami (1935*a*) show that, apart from cerium and neodymium, samarium and gadolinium are the most abundant of the

TABLE 18.4
CONTENT OF YTTRIUM IN IGNEOUS ROCKS

Rock	Y (g/ton)
Dunite (Goldschmidt and Peters, 1931 <i>b</i>).....	<8
Liparites and rhyolites (Goldschmidt and Peters, 1932 <i>a</i>).....	<8
Ultrabasics, southern Lapland (calculated from Sahama, 1945 <i>b</i>).....	0.8
Gabbros and dolerites, southern Lapland (calculated from Sahama, 1945 <i>b</i>).....	7.9
Granites, southern Lapland (calculated from Sahama, 1945 <i>b</i>).....	5.5
Syenites, southern Lapland (calculated from Sahama, 1945 <i>b</i>).....	7.9

even-numbered lanthanides and that erbium and ytterbium are the most deficient (see Table 18.1). Sahama and Rankama (1938) found that among the Archean granites of Finland the richest in the rare-earth metals usually belong to the youngest age groups. This result was confirmed by Sahama and Vähätalo (1939*b*), who also found that most of the granites investigated had a pronounced cerium maximum in the abundance graph of the lanthanides. However, in some granites the yttrium-earth metals were enriched. This shows that the abundance of the cerium-earth and the yttrium-earth groups may vary considerably. According to Sahama and Vähätalo, the lanthanides were altogether absent in gabbros and diorites. Nepheline syenites, in general, are rich in the cerium-earth metals (Goldschmidt, Hauptmann, and Peters, 1933).

The content of some of the cerium-earth metals in the various classes of igneous rocks is presented in Table 18.5. A comparison of Tables 18.4 and 18.5 shows that yttrium is enriched in basic rocks, compared with lanthanum, cerium, and neodymium. The reason is

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the calcium-yttrium diadochy; the substitution of Ca^{2+} by Y^{3+} is easier than the substitution by La^{3+} , Ce^{3+} , or Nd^{3+} .

CYCLE OF YTTRIUM AND THE LANTHANIDES

Like most other trivalent metals, yttrium and the lanthanides are collected, for the most part, in hydrolyzate sediments. Scandium, yttrium, and the lanthanides do not become collected in the residual bauxites, because their ionic potentials are lower than the potential of aluminum and, consequently, permit their removal in aqueous

TABLE 18 5
CONTENT OF SOME CERIUM-EARTH METALS IN IGNEOUS ROCKS

Rock	La	Ce	Nd
	g/ton		
Dunite (Goldschmidt, 1937a)	0		
Gabbro (Goldschmidt, 1937a)	9		
Diorite (Goldschmidt, 1937a)	26		
Granite (Goldschmidt, 1937a)	43		
Nepheline syenite (Goldschmidt, 1937a)	430		
Ultrabasics, southern Lapland (calculated from Sahama, 1945b)	0	0	0
Gabbros and dolerites, southern Lapland (calculated from Sahama, 1945b)	0	0	0
Granites, southern Lapland (calculated from Sahama, 1945b)	60	65	60
Syenites, southern Lapland (calculated from Sahama, 1945b)	51	49	26

solution. Because their hydroxides are stronger bases than aluminum hydroxide, they remain partly in solution during the weathering and the formation of the hydrolyzates. Such remains are carried down in the carbonate sediments. Therefore, limestones contain appreciable quantities of yttrium and the lanthanides diadochically replacing calcium. Goldschmidt (1937a) found all lanthanides and yttrium in the calcium carbonate of coral limestone. However, only traces of scandium are present. This circumstance is another proof of the fact that yttrium and the lanthanides, the cerium-earth metals in particular, form ionic solutions during weathering with a considerably higher degree of ease than scandium does.

Yttrium is notably concentrated in the insoluble residues formed during the solution of limestones and in calcareous shells of marine organisms.

The quadrivalent cerium probably follows thorium and scandium in its cycle, unlike the trivalent yttrium and lanthanides.

Hydrous carbonate and phosphate minerals of secondary origin of the rare-earth metals are known to exist, such as lanthanite, $(\text{La}, \text{Ce}, \dots)_2[\text{CO}_3]_3 \cdot 8\text{H}_2\text{O}$, which occurs in soil, and weinschenkite, $(\text{Y}, \text{Er})[\text{PO}_4] \cdot 2\text{H}_2\text{O}$, which is found as a coating on manganeseiferous limonite ores in Bavaria and in Virginia in the United States. According to Milton, Murata, and Knechtel (1944), the weinschenkite in Virginia was deposited from meteoric waters as a result of secular extraction of the rare-earth metals from clay by chestnut trees, con-

TABLE 18.6
CONTENT OF YTTRIUM IN SEDIMENTS AND THEIR DERIVATIVES

Material	Y (g/ton)
Bauxites (Goldschmidt and Peters, 1931b)	<8
Terrigenous mud (Goldschmidt and Peters, 1931b) . .	0
Red clay, average (Goldschmidt and Peters, 1931b) . .	<8
Radiolarian ooze (Goldschmidt and Peters, 1931b) . . .	0
<i>Globigerina</i> ooze (Goldschmidt and Peters, 1931b) . . .	<8
Manganese nodule (Goldschmidt and Peters, 1931b) . .	8
Glauconitic sandstone (Goldschmidt and Peters, 1931b)	<8
Sedimentary iron ores (Goldschmidt and Peters, 1931b)	usually 8-79
Sedimentary manganese ores (Goldschmidt and Peters, 1931b)	maximum 8
Quartzites, southern Lapland (Sahama, 1945b)	1.6
Aluminum-rich schists, southern Lapland (Sahama, 1945b)	15.8
Carbonate rocks, southern Lapland (Sahama, 1945b)	0

centration in chestnut leaves, deposition in soil, adsorption in limonite and psilomelane, and precipitation as phosphate.

The content of yttrium and the lanthanides in sediments and their derivatives is known very incompletely. What information is available is presented for yttrium in Table 18.6 and for lanthanum, cerium, and neodymium in Table 18.7. In the rocks of southern Lapland, yttrium is enriched in the hydrolyzates, which have received material from basic rocks. Cerium is evidently highly deficient in the hydrolyzate sediments of this area.

EUROPIUM

The abundance graphs presented in Figure 18.1 show that one the lanthanides, viz., europium, is nearly totally absent in the materials investigated. However, in stony meteorites and in shales the abundance of europium is nearly as high as, for example, the abun-

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dance of terbium. The presence of europium in the solar and stellar atmospheres has also been established, and actually it is an abundant element therein, as far as the lanthanides are considered. The explanation of the scarcity of europium in the rare-earth minerals is that it usually occurs in the bivalent state in Nature and consequently does not accompany the other lanthanides, which are trivalent, but becomes individually concentrated in other minerals. Because the radius of Eu^{2+} (1.24 kX) corresponds closely to the radius of Sr^{2+} (1.27 kX), it is natural to assume that europium follows strontium and is concentrated in minerals and rocks which are rich in this metal. Goldschmidt (1937*a*, *b*) has shown that actually some miner-

TABLE 18.7
CONTENT OF LANTHANUM, CERIUM, AND NEODYMIUM IN
METAMORPHOSED SEDIMENTS OF SOUTHERN
LAPLAND (SAHAMA, 1945*b*)

Rock	La	Ce	Nd
	g/ton		
Quartzites	17	24	17
Aluminum-rich schists	26	0	26
Carbonate rocks	0	0	0

als of strontium and lead (the radius of Pb^{2+} is 1.32 kX) contain noteworthy amounts of europium, compared with the amounts of the other rare-earth metals which may be present. Such minerals are strontianite, SrCO_3 , and pyromorphite, $\text{Pb}_5[\text{Cl}](\text{PO}_4)_3$, which sometimes contain up to 860 g/ton Eu. Among the rock-making minerals, sphene (up to 340 g/ton Eu) and the early-crystallized, strontium-rich potash feldspars (up to 17 g/ton Eu) are particularly rich in europium (Goldschmidt, 1937*b*). In like manner the lead-bearing feldspars may carry considerable amounts of europium. Bivalent europium is sometimes also concentrated in fluorite (maximum 400 g/ton Eu) and in calcite (up to 10 g/ton Eu). Goldschmidt (1939) reports 32 g/ton Eu in a carbonate rock of igneous origin. According to Haberlandt (1947), europium, along with other lanthanides, is present in uraninite. It is particularly enriched in the hydrothermal uraninites, but the uraninites of pegmatites are rather poor in europium. Likewise, the hydrothermal fluorites are rich in europium, but

the content in pegmatite fluorites is low. Also, some hydrothermal apatites are europium-bearing.

According to Sahama (1945*b*), the young granites of southern Lapland in Finland contain less than 0.9 g/ton Eu. In gneissose granites and granite gneisses of this area the content is 2.6 g/ton. No other information is available to show the europium content of igneous rocks.

In limestones, bivalent europium follows strontium and, consequently, replaces calcium in the calcite structure. During the weathering, bivalent europium is largely oxidized to the trivalent state and then follows the other lanthanides being precipitated in the hydrolyzates. Therefore, europium in shales is nearly as abundant as, e.g., terbium, as was shown by Minami (1935*a*). There is no other information available on the content of europium in sediments and their derivatives.

THE RARE-EARTH METALS IN THE BIOSPHERE

The rare-earth metals occur in small concentrations as temporary constituents of plants and animals. Their presence is reported in algae. With the exception of holmium, terbium, and lutecium, the rare-earth metals have been found in some plants, for example, in hickory and chestnut leaves and in tobacco and rice. They are also enriched in coal ashes (Goldschmidt and Peters, 1933*c*). The content of scandium in coal ashes may be 3 g/ton Sc; the content of yttrium is less than 8 g/ton Y (Goldschmidt and Peters, 1931*b*). The content of lanthanum in soil is up to 500 g/ton La, and the content of yttrium, similarly, up to 500 g/ton Y (Mitchell, 1944). The presence of the rare-earth metals has been established in bones, and scandium, at least, is found as a constituent of marine animals (Noddack and Noddack, 1940).

ABUNDANCE AND GEOCHEMICAL CHARACTER

CARBON differs chemically from all other elements by its property of being capable of forming more compounds than all the other elements together. The number of known compounds of all elements with the exception of carbon is about forty thousand, but that of carbon compounds is estimated to approach four hundred thousand. This peculiarity of carbon is caused by its atomic properties, in particular by its ability to form chains and rings of linked carbon atoms. The ultimate result is the formation of organic compounds with complex structures which are unrivaled among inorganic substances.

Carbon is cosmically both an abundant and a common element. The spectra of the stars belonging to classes R and N show very strong bands which are due to carbon molecules and carbon compounds. The atmospheres of such carbon stars are reducing because their carbon content is higher than the content of oxygen. The star R Coronae Borealis contains much carbon but only a little hydrogen. Carbon is one of the most abundant elements in the solar atmosphere. It acts as a catalyst in the nuclear reactions producing stellar energy (see chap. 2). The atmosphere of Venus contains large amounts of carbon dioxide, and methane is one of the chief constituents of the atmospheres of the giant planets. Carbon compounds are present in comets, and carbon is a constituent of the meteorites. The abundance of carbon calculated from Tables 1.3 and 2.3 for the meteorites and for igneous rocks is given in the accompanying tabulation.

Material	C (Per Cent)
Irons.....	0.08
Chondrites.....	0.16
Achondrites.....	0
Igneous rocks.....	0.08

Even though the distribution of carbon among the meteorite phases is not known in all details, carbon certainly is a definite con-

stituent of iron meteorites. It occurs in the meteorites chiefly as cohenite, Fe_3C , and often as graphite, whereas moissanite, SiC , diamond, and amorphous carbon are rare. Some chondrites are exceptionally rich in carbon. These facts show that carbon is geochemically a siderophile element. However, it is also lithophile and, in the form of carbon dioxide and methane, one of the atmophile elements. The most conspicuous geochemical feature of carbon, however, is its strong biophile character: it is a primary constituent of all living matter.

According to its electron configuration, carbon may occur in its compounds in the tetrapositive and tetranegative state. Because of the relatively high redox potential in the upper lithosphere, carbon nearly always forms complex $[\text{CO}_3]$ anions in igneous rocks. In the upper lithosphere carbon is definitely oxyphile. It is tetranegative in carbides, but in these compounds the bond is covalent or metallic.

CARBON IN IGNEOUS ROCKS

Primary igneous rocks contain carbon either in the native state (diamond and, rarely, graphite), as $[\text{CO}_3]$ groups in certain silicate and other minerals, or as independent carbonate minerals. Diamond is not uncommon as a constituent of certain ultrabasic rocks. It occurs as a product of deep-seated crystallization, particularly in the kimberlite pipes and volcanic necks in South Africa, and evidently it has been transported relatively rapidly by the ascending magmas from the lower levels of the lithosphere. It is considered to have been formed under high pressure. When occurring in igneous surroundings, graphite is mainly restricted to pegmatites and hydrothermal rocks. It is, however, a common constituent of metamorphic rocks, and usually it is formed from carbonaceous material of the sediments during metamorphism. In any case both graphite and diamond are rare, and therefore their role in the quantitative geochemistry of carbon is rather unimportant. Carbon in $[\text{CO}_3]$ anions occurs as an essential constituent of some silicate, phosphate, and other minerals. It is analogous to the chloride and sulfate anions in scapolite and apatite and in cancrinite, a constituent of alkalic rocks. Among these minerals, apatites are geochemically the most important. However, the most common apatites of igneous rocks are chlorapatites and fluorapatites, and carbonate apatites are rare.

The independent carbonate minerals represent the most important manner of occurrence of carbon in igneous rocks. Among them, cal-

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cite, CaCO_3 , is the most important species. According to Clarke (1924), the average CO_2 content of igneous rocks is 0.101 per cent by weight, but actually the content shows a wide range of variations. The carbonate ions tend to concentrate toward the last stages of magmatic crystallization. Veins of carbonate minerals are sometimes formed during the pegmatitic stage, and their number increases greatly when the pneumatolytic and hydrothermal stages of crystallization are reached. These veins carry carbonates of magnesium and iron along with calcium carbonate. Under exceptional conditions the residual solutions rich in water and carbon dioxide may produce primary igneous rocks which contain chlorite and siderite, FeCO_3 , as their main constituents.

The content of carbon in igneous rocks is relatively low, and it is evident that the bulk of carbon is not deposited in rocks formed during the main stage of crystallization but becomes concentrated in the residual solutions and combines with oxygen to form carbon dioxide and the anions of carbonic acid. When the supply of oxygen is not sufficient or when a partial reduction takes place, carbon monoxide is formed. The carbon oxides are constituents of volcanic emanations (see Table 5.38), which carry carbon dioxide as one of their main constituents; carbon monoxide is of less importance. The amount of carbon dioxide of juvenile origin which escapes into the atmosphere is very remarkable: $0.003 \text{ mg} \cdot \text{cm}^{-2}$ – $0.006 \text{ mg} \cdot \text{cm}^{-2}$ annually, according to the estimate of Goldschmidt (1933a; see under "Cycle of Carbon," p. 541). As a matter of fact, juvenile carbon dioxide is the most important source of carbon in its cycle. It is important to note, however, that only a part of the carbon dioxide brought to the surface in volcanic emanations is of true juvenile origin. Another part may have been released by the action of rock melt on rocks surrounding the center of volcanic activity. In fact, limestone beds often occur in the immediate neighborhood of volcanoes. The silica of the molten rock has metasomatically replaced the carbon dioxide of the carbonates, and thus silicates have been produced under the simultaneous liberation of carbon dioxide, which in this case is ultimately of meteoric origin.

CARBON IN THE BIOSPHERE

Carbon is the characteristic element of all organic substances. The carbon content of higher organisms is 15–20 per cent. The unique chemical properties of carbon referred to in the first paragraph of this

chapter are the cause of its dominant role in the biosphere. In living matter, carbon occurs chiefly in carbohydrates, lipides, and proteins. Notwithstanding the dominant role of carbon in the biosphere, its amount therein is surprisingly small.

The manner of occurrence of carbon in the biosphere was discussed in chapter 8.

CYCLE OF CARBON

The principal qualitative features in the cycle of carbon have long been known. The German chemist, Justus von Liebig (1803–73), was the first to emphasize, in 1840, the importance of the inorganic and biochemical processes involved therein; and Jean Baptiste André Dumas (1800–1884), the French chemist, presented, in 1841, the first general scheme of the cycles of carbon and nitrogen.

The cycle of carbon is presented in Figure 19.1, which is based on the diagrams presented by Goldschmidt (1933*a*, 1934), Noddack (1937), Eskola (1939), Kalle (1943), Fearon (1947), and on still other information. The main features of the cycle of carbon are the following:

Carbon dioxide is released by volcanic vents and hot springs. This carbon dioxide is partly juvenile and partly meteoric. A small part of it may react at low temperatures metasomatically with silicate rocks, thereby replacing the silica of silicates. Spilites and talc-carbonate rocks are formed as a result of this process. However, the greatest part of the carbon dioxide escapes into the atmosphere or becomes dissolved in water. During weathering, the carbon dioxide-bearing waters react chiefly with dissolved calcium salts to form calcium carbonate and calcium bicarbonate. Calcium carbonate is finally deposited by either inorganic or organic agents. The formation of limestone is the greatest leak in the cycle of carbon. It is evident that the carbon dioxide removed from the cycle by this process will never totally return into the atmosphere. Only negligible amounts of carbon dioxide are liberated during the silicification of the limestones, and therefore the quantity of the carbonate rocks is bound to increase, as pointed out by Högbom (1894). So far, the deficiency caused by the formation of carbonate sediments is covered by carbon dioxide produced by the volcanoes and by industrial activity.

Another part of the carbon dioxide is used by the green plants, which convert it into organic compounds by photosynthetic reduction (see chap. 8). Higher plants and algae release carbon dioxide by

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respiration in the dark concurrently with its absorption, and the net effect is production of carbon dioxide. Green terrestrial plants do not take the bulk of their carbon dioxide from the atmosphere but from soil in which the CO_2 content is considerably higher than in air. In tropical forests there actually occurs a local, more or less closed, par-

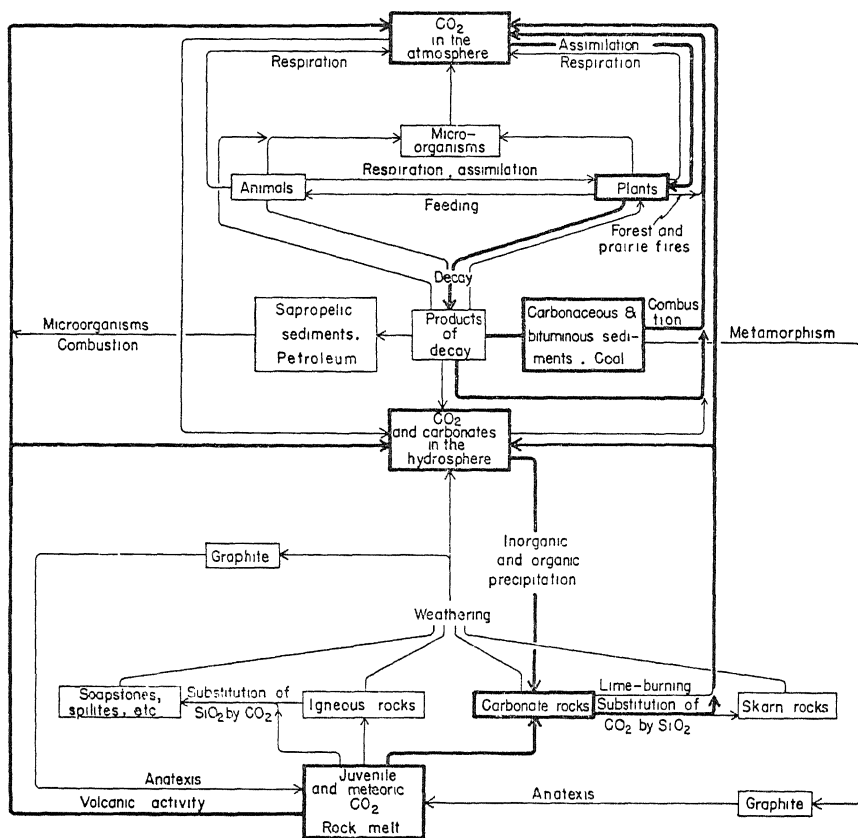


FIG. 19.1.—The cycle of carbon

tial cycle of carbon dioxide between soil and the leaves, and a similar partial cycle takes place in the sea. Therefore, the free atmospheric carbon dioxide is largely only a reserve supply, and many authorities believe that it is nothing but a residue from the partial cycle. Its content depends on the carbon dioxide equilibrium of the sea, contrary to the carbon dioxide found in soil. An increase in the carbon dioxide content of air goes ultimately for the benefit of marine algae, which, therefore, in this case will determine the partial pressure of carbon

dioxide in the surface layer of the sea. Thus industrial production of carbon dioxide (see the following paragraph) means increased productivity of the ocean.

A part of the vegetable carbon is consumed by animals and returns into the atmosphere mostly as carbon dioxide, a product of respiration. Methane is produced in bacterial fermentation. After the death of the plants, most of their carbon is oxidized to carbon dioxide and returns to the atmosphere, while another part may form hydrocarbons, e.g., methane, CH_4 , which is likewise released into the air, and the rest is only partially decomposed and forms peat or is deposited in sapropelic muds. In the course of time these muds are converted into carbonaceous and bituminous sediments. In like manner, animal remains give rise to sapropelic sediments. There occurs, accordingly, another deficiency in the cycle of carbon, and the coal and oil deposits formed during the course of geological time represent the leak in question. Increasing amounts of the caustobioliths, however, are burned into carbon dioxide in the anthroposphere, and this gas returns to the atmosphere to participate again in the cycle. This compensates, and even overcompensates, for the leak produced by the formation of caustobioliths. It should also be noticed that numerous bacteria, yeasts, and molds are able to attack petroleum hydrocarbons, which are mainly converted into carbon dioxide (ZoBell, 1946c). Even heavy residues, such as asphalt, are susceptible to the attack of these micro-organisms, and the process is not without significance in the cycle of carbon.

This discussion refers primarily to terrestrial plants and animals. With reference to aquatic organisms, it should be noticed that the plants use carbon dioxide dissolved in water. The carbon dioxide given off by animals and that produced by decay of the organisms subsequent to their death remain in solution. Consequently, there is an abundant supply of carbon dioxide available for the photosynthetic processes of diatoms and other algae. Also dissolved organic substances, such as humic complexes, are present in fresh and salt waters; but, on the whole, their nature is so far unknown.

The cycle of carbon in the sea is not completely closed. The carbon dioxide removed from sea water by the various organisms is utilized partly for their calcareous structures, but the bulk is consumed in the synthesis of organic compounds. In the second case most of the carbon returns to solution as carbon dioxide, and under oxidizing conditions all organic matter is completely oxidized, whereas under

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reducing conditions anaerobic bacteria generate various products of putrefaction. If the calcareous structures are dissolved, the carbon dioxide bound therein returns to solution. However, there is always some loss to the cycle because neither the dissolution of calcium carbonate nor the decomposition of organic matter is complete.

The quantitative cycle of carbon may be calculated if the carbon content in materials of the uppermost geochemical spheres is known. The first quantitative discussion concerning the cycle of carbon was presented by Högbom (1894), who emphasized the fact that the mass of carbon dioxide bound in carbonate sediments is so enormous that it cannot have existed in the primordial atmosphere but has been

TABLE 19.1
CONTENT OF CARBON DIOXIDE AND CARBON IN
SOME GEOCHEMICAL MATERIALS

MATERIAL	CO ₂	C
	g/ton	
Igneous rocks (Clarke, 1924). . . .	1,010	280
Sandstones (Clarke, 1924) . . .	50,400	13,800
Shales (Clarke, 1924)	26,400	7,200
Limestones (Clarke, 1924) . . .	415,800	113,500
Sea water (Noddack, 1937) . . .	50	14
Dry air (Table 7.1)	460	130

largely supplied, gradually, by volcanic emanations during the geological evolution of the Earth. He also thought that biochemical processes regulate the amount of carbon dioxide in the atmosphere and that the quantity of coal in the biosphere changes parallel to that of carbon dioxide in the atmosphere. The first quantitative cycle was calculated by Goldschmidt (1933*a*, 1934).

The carbon values necessary for the calculation of the cycle are presented in Table 19.1. When the mass of the sedimentary rocks and the masses of the hydrosphere and atmosphere are known in addition, the total amount of carbon dioxide and carbon may be calculated which has participated in the cycle of carbon during the geological evolution of the Earth, i.e., during the time of active weathering and formation of sediments. The masses needed for the calculation have been given previously (see chaps. 5, 6, and 7), and their application leads to the quantities given in Table 19.2. The distribution of carbon in the uppermost geospheres, with especial reference to the

biosphere, is presented in Table 19.3, which is based on Waksman (1936).

With reference to Table 19.2, it should be noticed that, according to Eskola (1939), Goldschmidt's value for limestones and dolomites is probably too small, perhaps even by an order of magnitude, because the carbonate sediments on the ocean bottom are not included therein. This remark is still more justified in the case of Kalle's values.

TABLE 19.2
CONTENT OF CARBON IN THE UPPERMOST GEOSPHERES

MATERIAL	CO ₂	C
	g · cm ⁻²	
Limestones and dolomites (Goldschmidt, 1933a)	6,562	1,791
Coal and bitumen (Wickman, 1941)	760	207
Hydrosphere (Buch, 1939b)	25	7
Atmosphere (Goldschmidt, 1933a)	0 4	0 11
Total	7,347 4	2,005 11
<i>Kalle (1943):</i>		
Sedimentary rocks (total):		2,968 7
Sandstones		263 6
Schists (shales and slates)		956 9
Limestones		1,748 2
Coal and petroleum		1,263 74
Hydrosphere		7 5
Atmosphere		0 125
Plants		0 053
Animals		0 00071
Total		4,240 11871

It is evident that the amount of carbon contained in igneous rocks is considerably smaller than that present in sediments and sedimentary rocks. Kalle (1943) estimates the total of carbon in igneous rocks as 1,180.87 g · cm⁻² C.

As was pointed out previously, volcanic activity has so far been the only source of additional carbon dioxide to the cycle of carbon. Eskola (1939) emphasizes the fact that juvenile carbon dioxide migrates continually toward the Earth's crust, obeying the same physicochemical laws as does granitic magma. Table 19.2 shows that considerably more than 7 kg · cm⁻² carbon dioxide has been added to the cycle during the geological history of the Earth as a result of volcanic activity.

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Supposing that the length of the geological time is $2,000 \cdot 10^6$ years, it may be calculated that a minimum of $0.0037 \text{ mg} \cdot \text{cm}^{-2} \text{ CO}_2$ is produced annually by volcanic activity.

Conway (1943) furnished rather conclusive proof of the validity of the opinion that juvenile carbon dioxide is the main source of this compound passing through and gradually added to the biosphere. Eskola (1939) pointed out that during orogenic periods in the Earth's history the volcanic activity and probably also the production of carbon dioxide have attained a maximum. Because orogenic periods are also culmination periods in biological evolution, it is natural to assume that the increased supply of carbon dioxide and the corresponding increase in the supply of oxygen have been at least one of the causes of the evolution of higher forms of life.

TABLE 19.3
DISTRIBUTION OF CARBON IN THE UPPERMOST GEOSPHERES

Source	C (Gg)
Hydrosphere	0.164
Atmosphere.....	0.006
Biosphere:	
Bituminous coal.....	0.02732
Brown coal.....	0.01499
Peat.....	0.01123
Anthracite coal.....	0.00422
Living matter.....	0.007
Topsoil.....	0.004

Estimates concerning the amounts of carbon dioxide and carbon consumed annually during the cycle were presented by Goldschmidt (1933a, 1934) and Kalle (1943). Their estimates are given in Table 19.4. The values recorded show the important role of biochemical phenomena in the cycle of carbon. However, with reference to Goldschmidt's estimates concerning the amounts produced by respiration and decay and consumed by photosynthesis, Buch (1942a) thinks that these values are too uncertain to indicate whether equilibrium exists between the production and the consumption of carbon dioxide. Buch (1945) also considers the annual consumption of $40 \text{ mg} \cdot \text{cm}^{-2} \text{ CO}_2$ by photosynthesis too great because the surface of the oceans is many times as great as that of the continents and vast areas of the ocean are practically sterile. However, it has been calculated that photosynthetic processes would be able to remove the total of the atmospheric carbon dioxide in less than ten years (see chap. 8).

As pointed out by Sauramo (1938), it is probable that graphite has a very much simpler cycle than such carbon, which passes repeatedly through the biosphere and the atmosphere. Graphite, whether of igneous origin or formed during the metamorphism of carbonaceous sediments, is not decomposed completely during the weathering but is redeposited in sediments, chiefly in hydrolyzates. During metamor-

TABLE 19.4
ANNUAL PRODUCTION AND CONSUMPTION OF CARBON DIOXIDE

PRODUCTION AND CONSUMPTION	CO ₂	C
	mg. cm ⁻²	
<i>Goldschmidt (1934):</i>		
Production of juvenile CO ₂	0 003-0 006	0.0008-0 0016
Production of CO ₂ by combustion of coal and petroleum	0 8	0.22
Production of CO ₂ by respiration and decay	~40	~10 92
Consumption of CO ₂ by photosynthesis	~40	~10 92
Consumption of CO ₂ by weathering	0 003-0 004	0.0008-0.0011
Consumption of CO ₂ by the formation of caustobiotoliths	0 0003-0 002	0.00008-0 0005
<i>Kalle (1943):</i>		
Production of CO ₂ by respiration		8.212
Production of CO ₂ by combustion of coal and petroleum		0.333
Production of CO ₂ by forest and prairie fires		0.314
Production of juvenile CO ₂		0.0042
Total production		8.8632
Consumption of CO ₂ by assimilation		8.530
Consumption of CO ₂ by deposition of vegetable and animal carbon in sediments		0.00297
Consumption of CO ₂ by the formation of coal and oil		0.00126
Total consumption		8.53423

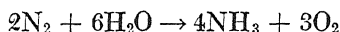
phism it recrystallizes, partly or entirely. Once formed, it is stable and follows a simple inorganic cycle.

It has been suggested (see chap. 27) that most, if not all, free oxygen in the present-day atmosphere has been formed as a result of the photosynthetic activity of green plants. The validity of this assumption can be quantitatively verified. It is evident that the present amount of free atmospheric oxygen and the amount once found in the air but now combined within the products of weathering (fossil oxygen) must correspond to the amount of carbon present in coal, petroleum, and other carbon-bearing biololiths according to the formula CO₂, i.e., as presented by the C:2O ratio. According to Table

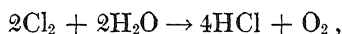
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19.2, the amount of carbon contained in coal and bitumen is about $0.21 \text{ kg} \cdot \text{cm}^{-2}$. The amount of oxygen needed to convert all this carbon into carbon dioxide is $0.55 \text{ kg} \cdot \text{cm}^{-2}$. According to Goldschmidt (1933*a*; see chap. 27), the amount of free oxygen in the atmosphere and in the hydrosphere plus the quantity of fossil oxygen present in sediments and their derivatives is $0.485\text{--}0.794 \text{ kg} \cdot \text{cm}^{-2}$. The higher estimate corresponds more closely to the known facts (see chap. 23). Accordingly, the grand total of free and fossil oxygen is of the same degree of magnitude as the amount needed to convert into carbon dioxide the fossil carbon of the bioliths and the carbon now found in the biosphere. It is evident that the amounts of carbon and oxygen correspond satisfactorily to the stoichiometric ratio between these elements as expressed by the formula CO_2 .

Actually, there is, according to the calculation presented above, an excess of oxygen over that required to convert the carbon of the biosphere and the fossil carbon into carbon dioxide. A part of the excess is accounted for by oxygen liberated in the reaction



(Hutchinson, 1944; see chap. 23) and another part by oxygen produced in the reaction between juvenile chlorine and water:



which Nichols (1941) claims to be a source of some atmospheric oxygen. So far, no calculations are available showing the amount of oxygen liberated in this reaction. As pointed out by Nichols, oxygen is also consumed in the oxidation of other substances contained in volcanic emanations.

CYCLE OF CARBON DIOXIDE BETWEEN THE ATMOSPHERE AND THE SEA

The cycle of carbon dioxide between sea water and the atmosphere forms a part of much geochemical interest in the general cycle of carbon. The phase boundaries water/air and water/ocean bottom are important in the geochemistry of carbon because an exchange of carbon dioxide between the hydrosphere and the atmosphere or the lithosphere takes place on these surfaces. The exchange is governed by laws of physicochemical reversible equilibrium. The carbon dioxide system in sea water was discussed in chapter 6; the exchange reactions are presented in Figure 19.2. It is evident that the equilib-

rium of carbon dioxide also affects the solution and precipitation of calcium carbonate (see chap. 15).

The exchange of gaseous carbon dioxide in the atmosphere and of dissolved free carbon dioxide in sea water obeys Henry's law. The law of mass action will determine the equilibrium in the carbon dioxide system in the sea. Several physical and chemical factors cause changes in the partial pressure of carbon dioxide in the surface layer. The partial pressure increases with rise in temperature and in salinity (due to evaporation), respiration, precipitation of calcium carbonate, and upward circulation. It is bound to diminish, owing to decrease in temperature and in salinity, photosynthetic activity, and solution of calcium carbonate. Consequently, the content of carbon dioxide and

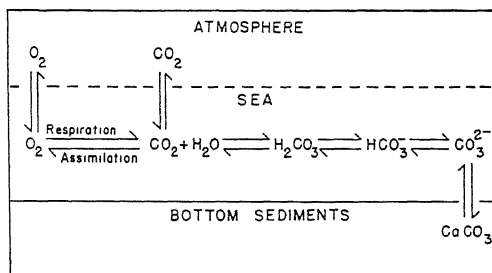


FIG. 19.2.—The carbon dioxide system in the sea

the concentration of the carbonate and bicarbonate ions vary considerably. Evidently, biological factors cause the fine adjustment in the partial tension of carbon dioxide, but they act only in connection with other factors, physical and oceanographic, such as the currents and the rotation of the Earth, and chemical, such as the concentration of oxygen and the nutrients. As pointed out by Krogh (1904a), bicarbonate-bearing river waters also cause changes in the carbon dioxide system of the sea.

All the factors discussed above also affect the carbon dioxide equilibrium between the sea and the atmosphere. Schloesing (1872) was the first to furnish experimental proof of the fact that the solubility of calcium carbonate depends on the content of carbon dioxide in the air in equilibrium with the aqueous phase. He (Schloesing, 1880) further emphasized the role of the ocean as a vast reserve containing carbon dioxide much in excess over the amount present in the atmosphere. Therefore, he suggested that the oceans regulate the carbon dioxide content of the atmosphere, being able to give off or absorb comparatively large quantities of this gas according to its partial ten-

sion in sea water. In like manner, Högbom (1894) considered sea water the regulating mechanism and thought that changes in the carbon dioxide content of the atmosphere are highly probable.

Krogh (1904*b*) found that the content of carbon dioxide in the atmosphere is rather variable. Although the action of factors diminishing the carbon dioxide content is fairly constant, the factors increasing the content are highly variable. These factors are volcanic and industrial activity. Krogh also believed in the regulating property of the ocean. In addition, he suggested that the content of carbon dioxide in the air is increasing because his analyses showed that the carbon dioxide tension in the surface water of the ocean is generally lower than the tension in the atmosphere, even though they are of the same degree of magnitude (about $3 \cdot 10^{-4}$ atm).

Buch (1934; 1939*a, b*; 1942*a, b*; 1945), in a series of papers, has offered a detailed explanation of the role of sea water as the regulating mechanism. According to Buch, the carbon dioxide system of the sea has attained, in the course of geological time, an approximate equilibrium with the atmosphere; but an exact equilibrium is rare, and changes occur which depend on temporary biological and physico-chemical factors. Because only a very small part of the total mass of the ocean is brought into contact with the atmosphere, a long time is necessary to produce the equilibrium. Air which remains in contact with sea water for several days attains practically the same partial tension of carbon dioxide as is found in the upper layer of the water. The changes in the partial pressure of carbon dioxide in sea water will determine the degree of regulation of the partial pressure in the atmosphere. Because very considerable changes in the carbon dioxide tension may take place in sea water, the ocean as a carbon dioxide regulator is rather changeable. However, compared with the atmosphere, the ocean is very slow in its changes. In addition, Buch found that in some parts of the ocean (Atlantic and Arctic) and in adjoining seas (Baltic) the changes in the carbon dioxide tension often are greater than in the atmosphere; and thus it would appear that the atmosphere regulates the carbon dioxide pressure of the ocean, not vice versa. Actually, both the atmosphere and the ocean regulate each other. Only the surface layer is available for the stabilization of changes in the carbon dioxide content of the atmosphere, which are temporary and of short duration, and therefore such variations cannot be controlled. On the other hand, a secular balance is maintained.

Buch also investigated the seasonal and geographic changes in the partial tension of carbon dioxide in sea water. The seasonal changes consist of a sharp decrease during the spring due to the growth of a vast population of diatoms. Thus, for example, during the growth of diatoms in the Gulf of Finland and in the Baltic the carbon dioxide tension decreases from its normal value of $3 \cdot 10^{-4}$ atm to $2 \cdot 10^{-4}$ atm, and additional carbon dioxide from the air is usually consumed during the whole summer. When the season of growth is over and the deep waters rise upward during the fall, the tension increases to $4 \cdot 10^{-4}$ or $5 \cdot 10^{-4}$ atm, and carbon dioxide is given off to the atmosphere. An equilibrium is attained during the winter.

Still following Buch: other areas are known in the sea in which carbon dioxide-rich waters constantly move in a certain direction, e.g., along the west coast of Africa and America. Owing to the rotation of the Earth, the surface layers move westward, being constantly replaced with CO_2 -rich waters from the depth. It is known that even at a depth of some hundred meters the partial tension of carbon dioxide may always be three times as high as the tension on the surface. The excess of the carbon dioxide is taken up by the air. Therefore, air in the trade-wind belts is rich in carbon dioxide. It migrates upward in the atmosphere and goes with the antitrades toward the north and the south. A part of the air charged with carbon dioxide is blown toward the surface in the polar regions and gives off its carbon dioxide to sea water, which during the summer months has a CO_2 tension of only $1.5 \cdot 10^{-4}$ atm. An equilibrium is therefore very nearly attained in Arctic waters during the summer months. The Arctic and Antarctic waters charged with carbon dioxide sink down and flow back toward the equator. During the winter the polar waters have a relatively high carbon dioxide tension due to the upwelling of deep waters in the fall. They are probably in equilibrium with the atmosphere. The absorption of carbon dioxide by sea water explains the fact that polar air is much poorer in carbon dioxide than air at lower latitudes.

CHANGES CAUSED BY INDUSTRIAL ACTIVITY IN CARBON DIOXIDE CONTENT OF THE ATMOSPHERE

It is of much geochemical interest that considerable amounts of carbon dioxide which result from the activities taking place in the anthroposphere are constantly being added to the atmosphere. Such carbon dioxide, mainly derived from the combustion of coal and pe-

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troleum and from thermal decomposition of limestone, forms an important addition to the cycle of carbon. On the basis of statistical data Goldschmidt (1933*a*) calculated that the amount of carbon dioxide liberated by the combustion of the above-mentioned fuels in 1929 amounted to $0.8 \text{ mg} \cdot \text{cm}^{-2}$. This amount does not include the carbon dioxide formed during the combustion of peat and wood, and therefore the grand total must be at least a hundred times as great as the amount produced by volcanic emanations (see Table 19.4). Moreover, considerable amounts of carbon dioxide are produced by the fermentation industry. According to Callendar (1940), the amount of carbon dioxide now produced by combustion is as high as about $300 \cdot 10^6 \text{ m}^3$ per hour. The figures presented in Table 19.2 show clearly that by far the greatest part of the juvenile carbon dioxide (about 90 per cent, according to Goldschmidt's figures) is stored away in carbonate sediments, while the remaining 10 per cent, or approximately $0.00037 \text{ mg} \cdot \text{cm}^{-2}$, is retained in the bioliths. If the fact is considered, in addition, that only a very small part of coal and petroleum deposits has any direct technical value and that by far the greatest part of carbon is contained in economically worthless muds, shales, and other carbon-bearing sediments and their derivatives, it is evident that the formation of new caustobioliths in Nature cannot compete with the constantly increasing rate of consumption of the fuel resources of the world. The conclusion is obvious that the natural fuels are being wasted; man acts like a ferment in the process of their consumption.

According to Noddack (1937), the grand total of the world's coal reserves is $5 \cdot 10^{12}$ tons, which, with an annual consumption of $4 \cdot 10^9$ tons, would last for twelve hundred years. According to chapter 8, the total yield of photosynthesis is approximately $15 \cdot 10^{10}$ tons carbon annually, or nearly forty times as high as the quantity of burned coal. However, even though the rate of formation of new bioliths thus is rapid, geological experience shows that even the formation of peat in most cases is too slow a process to produce new sources of fuel before the coal reserves have been depleted. In addition, the growing forests in many parts of the Temperate Zone are being cut down at a greater rate than new woods are being formed.

This discussion shows that the quantity of carbon dioxide added to the atmosphere by the combustion of caustobioliths is remarkable. The importance of man as a geochemical factor in this respect has already been realized by Högbom (1894) and Krogh (1904*b*). Buch

(1939*b*) calculated, on the basis of Goldschmidt's estimate of the amount of carbon dioxide liberated in 1929 by combustion of coal and oil (see above), that the content of carbon dioxide in the atmosphere would be doubled in five hundred years if the sea did not absorb any of this gas. However, provided that the sea absorbed carbon dioxide at the same rate at which it is produced by industrial activity, five-sixths of the annual increase would go into the sea and only one-sixth remain in the atmosphere. Therefore, the time required would be three thousand years; but even this estimate does not consider the effect of weathering, which will further increase the period required. This calculation shows that, in spite of the importance of man as a geochemical factor, the stability of the carbon dioxide content of the atmosphere is remarkable.

However, the content of carbon dioxide in the atmosphere is now on the increase. According to the analyses collected and published by Callendar (1940), the CO₂ content of the air in 1866–1901 was 292 parts per million (by volume); in 1909–12, 303 parts; and in 1932–35, 321 parts. The rate of the secular increase is consequently 29 parts per million, or 10 per cent. If the increase is assumed to have occurred throughout the whole atmosphere, then the additional carbon dioxide therein would amount to $20 \cdot 10^{10}$ tons. In 1900–1935 the total quantity of coal and oil burned was about $5 \cdot 10^{10}$ tons, which has given $15 \cdot 10^{10}$ tons carbon dioxide. Callendar attributes the difference, $5 \cdot 10^{10}$ tons, to incomplete mixing in the atmosphere because most of the carbon dioxide was added in the North Temperate Zone. In 1866–1900 the amount of carbon dioxide produced by the combustion of caustobioliths was relatively small, and its action on the composition of the atmosphere became noticeable only after that period.

According to Buch (1942*a, b*), an early-established equilibrium between the atmosphere and the sea was effective in regulating the amounts of carbon dioxide added to and subtracted from the atmosphere before the start of industrial activity on a vast scale. It is probable that the ocean and the atmosphere, at the beginning of the twentieth century, still had equal carbon dioxide tensions. After that period, water has not absorbed any considerable quantities of carbon dioxide, which consequently has remained in the atmosphere, increasing the carbon dioxide content therein by about 10 per cent—a result of the geochemical activities of the anthroposphere. Table 19.4 shows that, if Kalle's values are accepted, the total production

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of carbon dioxide is somewhat greater than the total consumption. The content in the atmosphere is still on the increase and will continue to be so until the pressure difference between the atmosphere and the sea has grown large enough and the rate of absorption thus increased sufficiently to produce equilibrium or a state at which carbon dioxide is absorbed as fast as it is produced. At the present time, the excess CO_2 pressure is only $2 \cdot 10^{-5}$ atm. When the above-mentioned state has been reached and the excess pressure has grown to about $3 \cdot 10^{-4}$ atm, the carbon dioxide content of the atmosphere will increase at a slower rate parallel to a corresponding increase of the partial pressure of carbon dioxide in sea water. However, hundreds, if not thousands, of years are required to establish the equilibrium between the atmosphere and the sea.

CARBON ISOTOPES

Five carbon isotopes are known. The isotopes C^{10} and C^{11} are artificially radioactive, as is C^{14} ; but, contrary to C^{14} , the two first-mentioned isotopes have very short half-lives. In addition, it is highly probable that C^{14} , or radiocarbon, is constantly being formed in Nature. The isotopes C^{12} and C^{13} are stable, and C^{12} is by far the more abundant of the two.

Nier and Gulbransen (1939) were the first to observe changes in the $\text{C}^{12}/\text{C}^{13}$ ratios of terrestrial materials. They found that C^{13} is concentrated in limestones, whereas plants prefer the light isotope, C^{12} . Murphey (1941) and Murphey and Nier (1941) confirmed these results. No age effect could be established. The first application of the isotope ratios to geochemical problems was the calculation of the amount of coal and bitumen carried out by Wickman (1941) (see Table 19.2).

Rankama (1948*b*) divided the materials analyzed with respect to their $\text{C}^{12}/\text{C}^{13}$ ratios into two general groups, inorganic and organic. He also suggested that the original isotopic composition of terrestrial carbon is that shown by meteorites. The ranges of the isotope ratio in these groups are shown in the accompanying tabulation. There

Group	$\text{C}^{12}/\text{C}^{13}$
Meteorites	89.8-92.0
Inorganic	87.9-90.2
Organic	90.3-93.1

seem to be, accordingly, two series of processes which change the original isotope ratio in two opposite directions. According to Kamen

(1946), isotope differentiation may be more characteristic of living than of inert systems. However, inorganic processes, thus far, have caused a more thoroughgoing fractionation than have the organic processes, even though inorganic fractionation seems to be slow compared with organic fractionation.

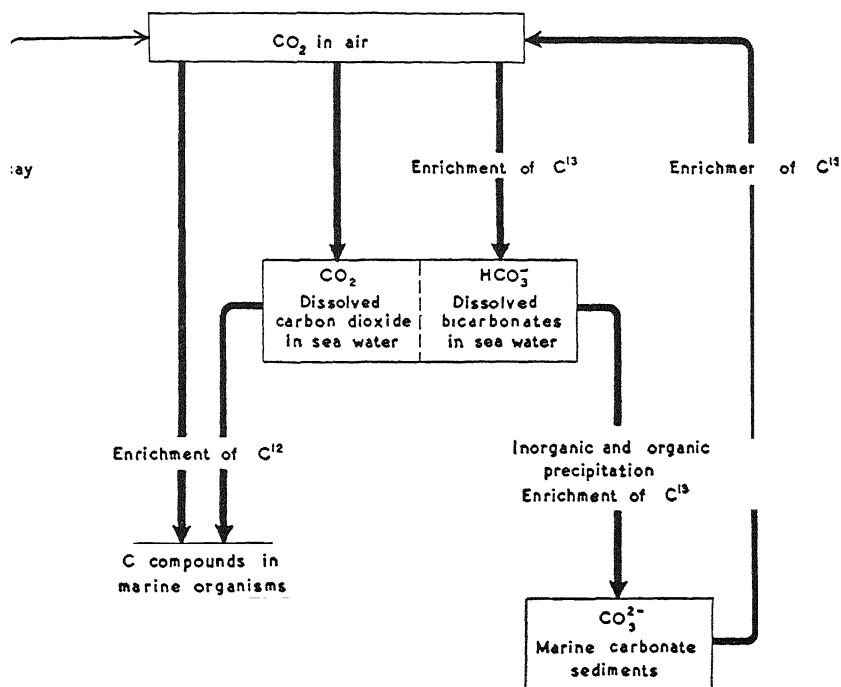
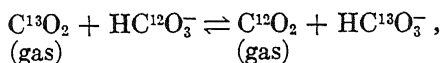


FIG. 19.3.—The cycle of the stable carbon isotopes between the atmosphere and the sea

Urey and Greiff (1935) studied reactions leading to a fractionation of the carbon isotopes. The most important reaction is



in which the equilibrium lies somewhat to the right. In the exchange between atmospheric carbon dioxide and the bicarbonate ion, the heavier isotope thus prefers to form the ion.

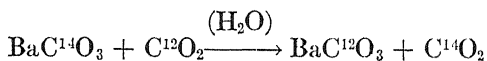
The above reaction is the basic one in the cycle of the carbon isotopes between the atmosphere and the sea. This cycle is presented in Figure 19.3 according to Rankama (1948b). The isotope C¹³ becomes enriched in sea water because of the exchange reaction presented

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above. During the formation of the carbonate sediments, either by inorganic or by organic precipitation, there probably occurs further enrichment of C^{13} . However, when the carbonate sediments are brought into contact with atmospheric carbon dioxide, their C^{13} content decreases. This conclusion is based on information presented by Armstrong and Schubert (1947), who found that $BaC^{13}O_3$ in the presence of water shows a definite exchange with atmospheric carbon dioxide (see below). The isotope C^{12} is enriched in marine plants and in animals feeding upon the plants. In the sea the lime-secreting organisms accumulate C^{12} in their organic substance, whereas C^{13} becomes concentrated in their shells. Nier and Gulbransen (1939) reported 88.7 for the value of the C^{12}/C^{13} ratio in a Recent clam shell, whereas the ratio in the clam flesh was 90.1. During and after the decay of the organisms a part of the carbon dioxide formed may reach the atmosphere. So far, it is unknown whether this process includes an enrichment of the isotope C^{12} .

Libby (1946) has suggested that neutrons produced by cosmic radiation form the carbon isotope C^{14} , along with tritium, H^3 , from nitrogen in the uppermost layers of the atmosphere. Anderson, Libby, Weinhouse, Reid, Kirshenbaum, and Grosse (1947) estimated that the total quantity of C^{14} in Nature is about 22 tons, or high enough to contaminate all carbon in living matter and in other forms in exchange equilibrium with the carbon dioxide of the air. They give $0.95 \cdot 10^{-10}$ per cent as the average content of C^{14} in living matter.

Armstrong and Schubert (1947) found that in the presence of water, the following exchange reaction takes place:



The half-life of C^{14} is probably 6,400–7,200 years.

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE abundance of silicon in meteoritic irons (calculated from Goldschmidt, 1937*b*), in silicate meteorites (Merrill, 1916; recalculated by Goldschmidt, 1937*b*), in igneous rocks (Clarke and Washington, 1924), and in argillaceous sediments (Minami, 1935*b*) is presented in Table 20.1.

TABLE 20.1
ABUNDANCE OF SILICON

Source	Si (Per Cent)
Meteoritic irons	0.004
Silicate meteorites	21.20
Igneous rocks	27.72
Argillaceous sediments	28.89

Silicon is a most typically lithophile element, which is nearly quantitatively contained in the silicate phase of the meteorites and in the silicate crust of the Earth. The amount of silicon in meteoritic irons is very small, and silicon either forms a solid solution with the metal phase or is present as the carbide, SiC, which is known as the meteorite mineral moissanite (see chap. 1). In silicate meteorites the abundance of silicon is second only to that of oxygen, and in the terrestrial igneous rocks the content of silicon is still greater, owing to the prevalence of feldspars and quartz with high silica content as compared with the meteoritic olivines and pyroxenes lower in silica.

In the Sun's atmosphere, silicon is likewise one of the most abundant elements (see Table 2.5).

SILICON IN IGNEOUS ROCKS

Silicon and oxygen are the elements most typical of the lithosphere. In the upper lithosphere, as in the silicate meteorites, silicon is, next to oxygen, the most abundant of all elements. The importance of silicon in the mineral kingdom is similar to that of carbon

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in organic compounds. In these compounds the carbon atoms are linked together and usually form long chains or closed rings. Silicon is similarly able to combine with oxygen to form groups of various kinds in the structures of minerals. The basic grouping is the silicon-oxygen tetrahedron, $[\text{SiO}_4]$; the tetrahedra are combined in a number of ways to form the frameworks of the silicate minerals (see chap. 5). Although silicon is the essential constituent cation in most minerals of petrological and geochemical importance, still it occupies only a very limited space in their structures. The radius of the Si^{4+} ion is very small (0.39 kX), and therefore silicon practically disappears among the big oxygen anions in the tetrahedra (see chap. 27).

In the lithosphere, silicon is evidently a typically oxyphile element.

The average chemical composition of the most important classes of normal calc-alkalic igneous rocks presented in Table 5.32 shows that silicon is strongly enriched toward the last phases of the main stage of crystallization. The silicon content is highest in the granites. However, petrological experience shows that the enrichment continues still further, because there is much quartz present in granite pegmatites and its crystallization goes on through the pneumatolytic and hydrothermal stages. The quartz veins of varying grades of purity are common in igneous and metamorphic terranes. The high degree of enrichment of silicon through the differentiation is often considered a measure of the progress of this phenomenon. Therefore, the order of the members of a differentiation series is often based on their silica content. However, this practice is not always legitimate because there are numerous rocks, for instance, in alkalic complexes, in which there is no regular change of the silica content in the differentiation series arranged according to the general geological principles established in the field. Thus two rocks, the one of which is clearly the differentiation product of the other, may have nearly equal silica contents. Such cases, even though rather common, are quantitatively unimportant.

The enrichment of silicon in the last products of magmatic crystallization is readily understood if the crystal chemical properties of the silicate minerals are considered. The minerals containing independent $[\text{SiO}_4]$ tetrahedra not linked by common oxygen ions usually have relatively stable structures. If the tetrahedra, on the other hand, share one or, particularly, more than one oxygen with neighboring tetrahedra, the distance between the silicon ions in question

must decrease. In this case the repulsive force between the highly charged Si^{4+} ions will increase consistently with the number of the oxygen ions shared by the tetrahedra, and therefore the stability of the structure will decrease. This is evidently the reason why two neighboring $[\text{SiO}_4]$ tetrahedra in silicates never share more than one oxygen ion. The most typical mineral in the structural group of the nesosilicates is olivine, $(\text{Mg,Fe})_2[\text{SiO}_4]$, which is also the most important constituent of the early differentiates of silicate magmas. According to its chemical composition, olivine belongs to the group of the orthosilicates, which are the poorest in silica of all the silicates. The feldspars, which, according to Clarke's (1924) calculations, are the most common constituents of igneous rocks (see Table 5.16), contain the bulk of the silica found in the upper lithosphere. They are structurally tectosilicates and usually crystallize at lower temperatures than do the olivines. Likewise, quartz is structurally a tectosilicate; it crystallizes at relatively low temperatures.

BIOGEOCHEMISTRY OF SILICON

Silicon is a universal structural constituent of plants; it is found particularly in the stems of horsetails and some grasses. The former may contain up to 80 per cent silica in their ashes. In plants very small amounts of silicon might be essential for the function of all cells. Vegetable silicon is probably a derivative of cellulose or other polysaccharides.

Silicon, probably as silica, is a characteristic structural constituent of the skeletons of many lower organisms. Diatoms are the only plants known to excrete silica. It is also secreted by the radiolarians. In addition, some fungi and the siliceous sponges have structural parts consisting of silica. In higher animals silicon occurs in all tissues, especially in connective tissues, but its content is very much lower than in plants. A sterol silicate is found in feathers.

According to Fearon (1947), silico-organic compounds might be expected to appear in place of certain carbon compounds, especially in plants, because of the close relationship between carbon and silicon.

CYCLE OF SILICON

During the weathering of silicate minerals silicon, like aluminum, is brought into ionic solution, usually in the form of alkali silicates. If the weathering solutions become concentrated, silica is precipitated as an amorphous gel, e.g., in arid regions. If only a silica hydro-

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sol is formed during the concentration of the solutions, it may migrate farther, because it is very insensitive to the flocculation caused by electrolytes in solution. Additional stabilization may also be caused by protective colloids, which are mostly of organic origin. Silica in solution may also react with other substances. Thus, e.g., mica-like clay minerals, such as kaolinite, halloysite, and montmorillonite, may be formed from silica and alumina, and also feldspar, mica, and zeolites of sedimentary origin are known.

The solubility of silica depends on the pH of the solution. The higher the pH, the more silica goes into solution. If the pH decreases, for instance, by the addition of carbon dioxide, silica is precipitated. This process may sometimes lead to a notable concentration of silica. Usually the carbon dioxide is the result of decay of organic substances.

Gruner (1922) has found that the less silica a silicate mineral contains, the greater will be the amount of silica dissolved in weathering solutions during the presence of dilute acids. Magnesium salts (sea water) were found to accelerate the solution of silica. In solutions containing organic protective colloids, silica, which is negatively charged, is precipitated by the action of cations or positively charged colloids. However, this precipitation is rather slow and often evidently incomplete. The organic protective colloids may also be decomposed by bacteria, whereupon silica is precipitated.

The abundance values of silicon in Table 20.1 show that the argillaceous sediments, on an average, contain somewhat more silicon than do the igneous rocks. The difference, although not very pronounced, is evidently due to the fact that, when ions of the alkali metals, calcium, and magnesium are extracted from the mineral structures during the weathering and when the clay minerals are formed, the amount of water incorporated in the new structures is less than the amount of the said cations in the original ones. Therefore, silicon becomes somewhat enriched in argillaceous sediments. However, Goldschmidt (1937*b*) points out that a certain portion of silicon, although small, might originally be contained in thermal waters, which deliver it directly to the Earth's surface.

The concentration of silicon in the resistates is very pronounced. The sandstones form the most typical group among these sediments. The average composition of the sandstones as calculated by Clarke (1924) reveals a content of 78.66 per cent SiO_2 , whereas the corre-

sponding content in igneous rocks, according to Clarke and Washington (1924), is only 59.14 per cent (see Table 2.1). In addition, sandstones with 70–90 per cent SiO_2 are common. The enrichment of silicon in the resistates is readily explained by the high stability of quartz, among all common rock-making silicate minerals, against mechanical and chemical disintegration. Quartz may consequently become enriched in the resistates as a result of purely mechanical processes. The other crystalline polymorphs of SiO_2 —tridymite and cristobalite—are rare and therefore do not possess much geochemical importance. Silica cannot further decompose chemically during the weathering. Although it may dissolve as silicate anions or as a hydro-sol, the amounts brought into solution by these processes are relatively small as compared with those produced during the weathering of most silicate minerals. It must also be taken into account that quartz has no cleavage which would promote its mechanical disintegration. Therefore, quartz is the most typical constituent of all continental resistates. Many sandstones are dominantly composed of quartz, and the quartzites are often nearly monomineralic. A part of quartz is ground to a fine powder during the transportation processes; it is finally deposited in the hydrolyzates, i.e., in geochemically irrelevant surroundings.

The bulk of silicon, perhaps more than 95 per cent, remains in the solid products formed during the weathering, and only a small portion is brought into solution. Fresh waters and sea water contain silicon in true or colloidal solution. According to the values presented in Tables 6.7 and 6.17, the silicon content of the salts of river waters and sea water is the following:

Material	Si (Per Cent)
Dissolved solids in river water.....	5.45
Dissolved solids in sea water	0.00006–0 01

These values show that there is a considerable content of silicon in river water, whereas ocean water contains only very little silicon. The fluctuations in the silicon content in sea water are due to the role of silica as a structural constituent in the shells of certain marine organisms.

Calcium is removed fairly completely from the sea by precipitation as calcium carbonate. Silicon is analogous to calcium in this respect, being deposited in the seas as silica. Vast amounts of silica sediments are thus formed which geochemically resemble carbonate

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sediments. However, there is no evidence of inorganically precipitated silica in recent marine sediments, and therefore the inorganic deposition of silica in sea water is geochemically unimportant. In this respect the marine siliceous sediments differ from the corresponding carbonate sediments. The formation of the siliceous sediments takes place in the sea through the action of both plants and animals, viz., diatoms, radiolarians, and sponges. The organic separation of silica has already started in fresh waters, in which rather pure siliceous sediments (diatomite with more than 90 per cent SiO_2) may become deposited. In sea water the rest of silicon is captured by the organisms mentioned above, and thus the surface layers become depleted of silicon. A part of the silicon removed from sea water by biological processes may return to solution after the death of the capturing organisms. During the decomposition of proteins, ammonia may be produced in excess of carbon dioxide and may increase the pH of the solution locally. Alkaline solutions are able to redissolve silica, which in this respect differs from calcium carbonate, which is dissolved in acid solutions and reprecipitated from alkaline ones.

The deposition of siliceous remains of organisms must be sufficient to balance the supply of silica by rivers to the sea. The siliceous remains are important constituents of marine sediments (diatom ooze and radiolarian ooze), although they are of less geochemical moment than the marine carbonate sediments are. Diatomite and radiolarite are formed during the induration from the corresponding oozes.

A common feature of all siliceous deposits is their aqueous origin. Inorganic siliceous deposits are formed by precipitation from thermal waters, which are often rich in silica. Silica is deposited from juvenile waters in geysers and hot springs as siliceous sinter (geyserite) and other spring deposits, which may often form beds of geological importance, even though they are geographically not very extensive. Other, chiefly inorganic, siliceous precipitates (chert, flint, jasper) are very common in the geological column. It might be possible that thermal waters carry a part of their silica directly to the sea, whereby the silicon content of sea water is bound to increase.

TITANIUM, ZIRCONIUM, HAFNIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

THE elements most closely related to silicon in the Periodic System, viz., titanium, zirconium, and hafnium, all belong to the group of the trace elements, but they are among the most abundant members of this group. Titanium is the most abundant of all the trace elements. According to Table 2.3, the average content of titanium in igneous rocks is 0.44 per cent, which is roughly one-fifth the content of magnesium. Zirconium and, particularly, hafnium are much scarcer, but they are, at any rate, more abundant than most of their neighbors in the Periodic System. The abundance of the three elements discussed is presented in Table 21.1.

The metal phase of the meteorites contains small amounts of the three elements, but their abundance in the sulfide phase is still unknown. The values recorded in Table 21.1 show that there are eighteen times as much titanium in the silicate phase as in the metal phase. In the eucrites, which are silicate meteorites with a gabbro-like composition, the titanium content is twice as high as in the common chondrites. In this respect the eucrites and the chondrites behave like the terrestrial gabbros and ultrabasics.

Because the three elements are nearly quantitatively concentrated in the silicate phase of the meteorites, it follows that they are all lithophile. This property is particularly strong in zirconium and hafnium.

The atomic abundance ratios of the three elements in igneous rocks, in silicate meteorites, and also in the solar atmosphere are rather similar (see Table 2.3). This is a proof of the fact that these elements are notably similar as far as their general geochemical character is considered.

Bands of titanium oxide are present in the spectra of most of the cooler stars, and some stars display strong bands of zirconium oxide. The cause of the presence of such bands is still unknown.

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Titanium, zirconium, and hafnium are strongly oxyphile in the upper lithosphere.

TITANIUM MINERALS

Titanium forms a number of independent minerals in rocks. In addition, it is concealed in the structures of many of the petrologically important minerals. According to Sahama (1946), titanium is intermediate between the cations, which never form independent minerals in common igneous rocks, being always concealed in the structures of other minerals, like rubidium, strontium, and barium, and those forming such minerals, for example, zirconium in zircon.

TABLE 21 1
ABUNDANCE OF TITANIUM, ZIRCONIUM, AND HAFNIUM

MATERIAL	Ti	Zr	Hf
	g/ton		
Metal phase of meteorites (Ti: Ishibashi, 1931; calculated by Goldschmidt, 1937 <i>b</i> . Zr: Noddack and Noddack, 1930)	100 unknown	8 unknown	unknown unknown
Sulfide phase of meteorites			
Silicate phase of meteorites (Ti: Hevesy, according to Goldschmidt, 1937 <i>b</i> . Zr: Hevesy and Wurstlin, 1934, recalculated by Goldschmidt, 1937 <i>b</i> . Hf: Noddack and Noddack, 1930)	1,800	95	1
Igneous rocks (Ti: Goldschmidt, 1937 <i>b</i> . Zr: Hevesy and Wurstlin, 1934. Hf: Goldschmidt, 1937 <i>b</i>)	4,400	220	4 5
Igneous rocks, average, Dutch East Indies (van Tongeren, 1938).		230	

The bulk of titanium found in the independent titanium minerals is present as Ti^{4+} ions. It must be emphasized, however, that the determination of the state of oxidation of titanium in minerals is usually difficult, particularly when the content of this element is low, i.e., when it is concealed in mineral structures. In the presence of both ferrous and ferric iron, trivalent titanium cannot be analytically distinguished from quadrivalent titanium. Therefore, the information on the occurrence of Ti^{3+} in minerals is, so far, incomplete. According to Jakob and Parga-Pondal (1932) and Jakob (1937), some phlogopites and biotites contain trivalent titanium. It is also possible that trivalent titanium rather than quadrivalent is present in pyroxenes and amphiboles.

Ilmenite, FeTiO_3 , rutile, TiO_2 , and sphene (also called titanite),

$\text{CaTi}[(\text{O}, \text{OH}, \text{F})|\text{SiO}_4]$, are the most abundant of the independent titanium minerals. Ilmenite contains 52.7 per cent TiO_2 and sphene 41 per cent. The three minerals are found as accessory constituents of many rocks. It is evident that the oxide minerals carry a considerable, if not the largest, part of the titanium present in the upper lithosphere. According to the calculations carried out by Hevesy, Alexander, and Wüstlin (1930), ilmenite is by far the most abundant independent titanium mineral in igneous rocks. The corresponding magnesium and manganese compounds—geikielite, MgTiO_3 , and pyrophanite, MnTiO_3 —are rare (see chaps. 14 and 31). Possibly more than 90 per cent of the total quantity of all titaniferous constituents of igneous rocks consists of ilmenite. Therefore, ilmenite is the actual carrier of titanium in these rocks, and the titanium quantities contributed by rutile and sphene are of much less importance. This result is readily understood because the oxide minerals of iron are very common accessory constituents of all igneous rocks and because, according to Ramdohr (1940), ilmenite is nearly as abundant as magnetite among the opaque oxides in igneous rocks. Ramdohr also stated that the bulk of titanium in a slowly crystallizing magma rich in volatile constituents becomes incorporated mainly in ilmenite and magnetite and sometimes in rutile, whereas only a small amount goes into silicate minerals, such as hypersthene and biotite. In volcanic rocks much titanium is present in augite, and, on the whole, the amount of titanium in silicate structures is greater than in plutonic rocks.

The manner of occurrence of titanium in igneous rocks is characterized by its tendency to become incorporated in oxide minerals. Along with ilmenite and rutile, the following oxide minerals of titanium are the most important:

Titanian magnetite (titanomagnetite),	$\text{Fe}(\text{Fe}, \text{Ti})_2\text{O}_4$
Perovskite,	CaTiO_3
Anatase,	TiO_2
Brookite,	TiO_2

Titanian magnetite is present only in rapidly solidified effusive rocks as a homogeneous mineral. In other igneous rocks it is decomposed to magnetite, ilmenite, and hercynite. Perovskite occurs mainly in basic alkalic rocks. Anatase and brookite are considerably less common than rutile. Titanium is also found, particularly in pegmatites, as various multiple oxides containing columbium, tantalum (see chap. 26), calcium, the rare-earth metals, etc. These minerals

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are usually rather complicated chemically, and they are of minor importance as far as the geochemistry of titanium is considered.

Unlike zirconium, titanium does not form the simple silicate, TiSiO_4 . Thermochemical studies have revealed that there exists no binary compound in the system TiO_2 - SiO_2 . The metasilicate, TiSi_2O_6 , is similarly unknown. The only silicates of titanium are complex silicates containing some other cation with a co-ordination number differing from that of Ti^{4+} . The only cations which need to be considered in rocks are Ca^{2+} , Na^+ , and K^+ , because only they are abundant enough, as pointed out by Sahama (1946). Because the heat of formation of calcium compounds is generally higher than that of the sodium and potassium compounds of corresponding composition, titanium is preferentially combined with calcium to form sphene. The sodium-titanium silicate ramsayite, $\text{Na}_2\text{Ti}_2[\text{O}(\text{SiO}_4)_2]$, replaces sphene in some alkalic rocks. The syenites and nepheline syenites, and particularly their pegmatites, contain a number of complicated Na-Ca-Ti silicates, many of which carry rare-earth metals.

Sphene is an important carrier of a number of elements, e.g., columbium, tantalum, and the rare-earth metals (see chaps. 18 and 26). Both cerium earths and yttrium earths may dominate in sphene. This mineral serves as an indicator of the bulk composition of the rare earths in the rocks (Sahama, 1946). The yttrium earths characterize granites, whereas the cerium earths are usually enriched in nepheline syenites. This distribution of the rare-earth metals is also shown by the lanthanide composition of sphenes extracted from these rocks. According to their ionic radii, the yttrium-earth metals are incorporated more readily in the sphene structure than are the cerium-earth metals.

Titanium is also concealed in the structures of most femic rock-making minerals. Varieties are known of nearly all dark minerals of igneous rocks which contain exceptionally high quantities of titanium. These minerals, which often have been considered independent species, include titanian garnet, biotite (wodanite), augite, amphibole, etc., with the exception of tectosilicates, in which titanium is not incorporated. Geochemically speaking, such titanian minerals are scarce. The highest titanium contents reported are 8.97 per cent TiO_2 in titanian augite (Lebedev and Lebedev, 1934) and around 12 per cent TiO_2 in wodanite. Small amounts of titanium are regularly incorporated in the structures of femic minerals, but these minerals are different from the titanian varieties proper. Pyroxenes, amphi-

boles, and biotite are quantitatively the most important among these minerals. Biotite may contain up to 1.5 per cent TiO_2 , the iron-rich varieties (lepidomelane) of alkalic rocks as much as 4.5 per cent. Up to 1.3 per cent TiO_2 may be present in hornblende and 0.7 per cent in augite.

It must also be noticed that titanium, according to its ionic properties, may occupy an entirely different structural position. Referring to the chemical relationship between silicon and titanium, it was previously believed that titanium replaces silicon in silicate structures. According to the present views in crystal chemistry, it is actually possible that titanium replaces silicon diadochically in the silicon-oxygen tetrahedra. On the basis of extensive research Kunitz (1936) concluded that this manner of replacement is the most common and, geochemically speaking, the most important in silicates containing titanium. However, owing to the notable difference in the radii of the Si^{4+} (0.39 kX) and Ti^{4+} (0.64 kX) ions, the replacement must be limited. So far, the manner of occurrence of titanium in silicate structures is known rather incompletely. According to Kunitz, the Ti-Si diadochy, which predominates in silicate minerals, occurs particularly in garnets, amphiboles, and micas. In a similar way the small amounts of titanium present in olivine would be incorporated in the silicon-oxygen tetrahedra. However, titanium is present in the minerals mentioned above, particularly in augite, also as Ti^{3+} ions with a radius of 0.69 kX and a co-ordination number 6. They may replace Al^{3+} (radius 0.57 kX), Fe^{3+} (radius 0.67 kX), and, in part, also Mg^{2+} (radius 0.78 kX). Kunitz suggested that the orthosilicates with the simplest possible silicon-oxygen frameworks contain all their titanium in the silicon-oxygen tetrahedra, whereas the silicates with more complicated frameworks may partly accommodate titanium outside the silicon-oxygen structure. However, recent crystal chemical studies have revealed that the Si-Ti diadochy might be of less importance for the manner of occurrence of titanium and that the bulk of titanium would replace aluminum, ferric iron, and magnesium in the structures of minerals.

TITANIUM IN IGNEOUS ROCKS

Titanium belongs to the iron family of the elements (Goldschmidt, 1929) or the ferrides (Landergrén, 1943; see chap. 33). Like iron, titanium shows a distinct tendency to become separated from the crystallizing magma at an early stage. It is enriched in the early crys-

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tallates as ilmenite and titanian magnetite. However, these minerals—the main constituents of titaniferous iron ores—might not become separated so early as previously suggested. The titaniferous iron ores are the most important magmatic surroundings of titanium, and their formation is one of the principal features of the geochemistry of this element. Many geologists consider the presence of titanium in an iron ore a proof of the primary magmatic origin of the ore body in question. However, according to Landergren (1948), several features contradict the primary endogenic relationships between titaniferous iron ores and basic igneous rocks, and it might be possible that a single principle does not govern the formation of these ores. Landergren concludes that at least some of the titaniferous iron ores result from the co-operation of exogenic enrichment of iron and titanium in hydrolyzate and oxidate sediments, with subsequent metamorphism and anatexis.

In rocks belonging to the main stage of crystallization, ilmenite is partly replaced by sphene. Rutile is rare in igneous rocks; it is found preferentially in rocks derived from the mother-liquors of gabbroic magmas, e.g., gabbro pegmatites.

The alkalic rocks and particularly their basic varieties are the richest in titanium. In contrast to the calc-alkalic rocks, the alkalic rocks often contain titanium concentrated in their pegmatites in the form of complex titanium silicates of calcium and the alkali metals, e.g., astrophyllite, $(K_2, Na_2, Ca)(Fe, Mn)_4(Ti, Zr)[OH | Si_2O_7]_2$, lamprophyllite, $Na_3Sr_2Ti_3[(O, OH, F) | (SiO_4)_2]_2$, with up to 30 per cent TiO_2 ; and rinkite, $Na(Ca, Ce)_2(Ti, Ce)[F | (SiO_4)_2]$. In the basic alkalic rocks the titanian garnet melanite, $Ca_3Fe_2[SiO_4]_3$, with Ti substituting for Si and NaTi for CaFe, replaces these silicate minerals. It is reported to contain up to 22 per cent TiO_2 , but an intergrowth of melanite and sphene may occur, which leads to some of the high titanium contents observed (Mackowsky, 1938). The melilite-bearing rocks contain perovskite (with 59 per cent TiO_2) as a characteristic constituent.

In the calc-alkalic rocks, which are the most abundant among the igneous rocks and consequently the most important geochemically, titanium becomes decidedly enriched in the first products of the main stage of crystallization, as appears from the average chemical composition of these rocks, calculated by Daly (1933; see Table 5.32). Titanium is also enriched in the residual liquors from the crystallization of basic rocks, e.g., in gabbro pegmatites.

TITANIUM, ZIRCONIUM, HAFNIUM

According to Clarke and Washington (1924), the average titanium content of igneous rocks is 6,400 g/ton. Hevesy (1932) gives a figure of a similar degree of magnitude, viz., 6,100 g/ton. These values, according to Goldschmidt (1937*b*), are definitely too high, owing to the large amount of rare basic rock types rich in titanium included in the material analyzed. Therefore, one must conclude that no reliable average exists which shows the abundance of titanium in igneous rocks.

CYCLE OF TITANIUM

The soluble salts of titanium are readily hydrolyzed. During the weathering, titanium consequently remains largely in the resistates. The most important rock-making titanium minerals, particularly ilmenite and rutile, are stable against weathering, and consequently they remain unchanged in the resistate sediments. Sphene is also often found therein. However, much titanium from the sphene goes into solution but is ultimately reprecipitated as brookite. This mineral, along with rutile and anatase, is also produced during the weathering of ilmenite. Titanium contained in the structures of femic minerals (pyroxenes, amphiboles, micas, etc.) is brought into solution during the weathering, but it is promptly hydrolyzed and carried into the hydrolyzates. Bauxites and laterites may contain as much as 4 per cent Ti; it is present therein as sphene, ilmenite, brookite, and probably also as anatase (Frederickson, 1948).

The content of titanium in sediments and their derivatives is shown in Table 21.2. The values for the southern Lapland rocks show the low content of titanium in resistates as compared with the hydrolyzates. Compared with the general titanium average of the upper lithosphere, viz., 4,400 g/ton Ti, only the laterites show a concentration of titanium. Landergren (1948) reports as much as 70,000 g/ton Ti in the Irish laterite ores.

Highly metamorphosed schists of sedimentary origin do not contain sphene. Titanium is present as oxide in these rocks (Sahama, 1945*b*).

TITANIUM ORES

Titanian magnetite, ilmenite, and rutile are the only minerals of titanium of economic importance. Rutile deposits are rare. In some iron ores hematite may be the main carrier of titanium, as was shown by Landergren (1943). The greatest and economically the most important titanium ore bodies are found in North America, India, Australia, and Norway. They all belong to the early-separated

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oxides. These ores are connected with basic rocks, particularly gabros and norites, and they are differentiation products of basic magmas. There are, in addition, technically important beach deposits consisting of ilmenite and rutile, which occur in the company of other heavy minerals, such as monazite and zircon. Some sands are mainly composed of ilmenite. Rutile is sometimes met in commercial amounts in syenite pegmatites and in apatite veins found in connection with nepheline syenites. Some bauxites are potential commercial sources of titanium.

TABLE 21.2

TITANIUM CONTENT OF SEDIMENTS AND THEIR DERIVATIVES

Rock	Ti (g/ton)
Quartzites (resistates), southern Lapland (Sahama, 1945 <i>b</i>) . .	960
Aluminum-rich schists (hydrolyzates), southern Lapland (Sahama, 1945 <i>b</i>)	6,300
Sandstones, Scania (Palmqvist, 1935; recalculated by Lander- gren, 1948)	4,400
Siderites, Scania (Palmqvist, 1935; recalculated by Lander- gren, 1948)	2,100
Oolites, Scania (Palmqvist, 1935; recalculated by Lander- gren, 1948)	5,000
Bog ores, Finland (Landergren, 1948)	1,500
Laterite-bauxite ores, northern Ireland (Landergren, 1948) .	32,500
Marine oolitic-siliceous iron ores (Landergren, 1948)	3,900
Marine siderite ores (Landergren, 1948)	2,000
Quaternary clays, Norway (Goldschmidt, 1933 <i>a</i> , 1937 <i>b</i>)	4,700
Shales, average (Minami, 1935 <i>b</i>)	4,300
Hydrolyzate sediments, average (Goldschmidt, 1937 <i>b</i>)	4,600

ZIRCONIUM MINERALS

Even though zirconium, according to its position in the Periodic System, resembles titanium chemically in many respects, the two elements differ from each other considerably in their manner of occurrence. Zirconium is found in minerals exclusively as the Zr^{4+} ion. Its radius (0.87 kX) is considerably bigger than the radius of Ti^{4+} (0.64 kX), and therefore its co-ordination number in regard to oxygen differs from that of titanium. Titanium most usually occurs in 6-co-ordination, whereas the co-ordination number of zirconium is 8. However, the co-ordination number 8 is evidently too high with respect to the size of the Zr^{4+} ion, and actually the tetrapositive zirconium should lie near the border line between 6- and 8-co-ordination—in fact, close to the border line on the 6-co-ordination side. Like titanium, 6-co-ordinated zirconium is unable to form a simple silicate, and therefore it is incorporated, 8-co-ordinated, in an orthosili-

cate (zircon). Actually, the co-ordination number 8 of zirconium is unnatural and leads to the fact that the zircon structure is not exceedingly stable and therefore cannot form during the early stages of crystallization. The instability of zircon also causes the existence of zircons of exceptionally low specific gravity, called zirconoids; they are metamict (see chap. 5).

Unlike titanium, zirconium forms a stable simple orthosilicate, $\text{Zr}[\text{SiO}_4]$, which is found in rocks as zircon. This mineral, with a ZrO_2 content of 67 per cent, evidently carries most of the zirconium present in igneous rocks. It is the only zirconium mineral of geochemical importance. The oxide, ZrO_2 , occurs in Nature as baddeleyite, but this is a rare mineral, entirely differing from rutile, which is common, and it is restricted in its occurrence to granites and their pegmatites. Consequently, it is without any geochemical importance. Like titanium, zirconium forms in alkalic rocks, and particularly in their pegmatites, a number of complex silicates with a complicated chemical composition, e.g., eudialite, $(\text{Na}, \text{Ca}, \text{Fe})_6\text{Zr}[(\text{OH}, \text{Cl}) | (\text{Si}_3\text{O}_9)_2]$; l  venite, $(\text{Na}, \text{Ca}, \text{Mn})_3\text{Zr}[\text{F} | (\text{SiO}_4)_2]$; and catapleite, $\text{Na}_2\text{Zr}[\text{Si}_3\text{O}_9] \cdot \text{H}_2\text{O}$. Catapleite is the richest in zirconium, containing 30–32 per cent ZrO_2 ; but none of the three minerals, being rare, has much geochemical moment. It must also be noticed that some zirconium is incorporated in the femic constituents of igneous rocks, but the contents are lower than those of titanium. As much as 0.4 per cent ZrO_2 is present in aegirite.

ZIRCONIUM IN IGNEOUS ROCKS

The differences in the manner of occurrence of titanium and zirconium are best illustrated by the behavior of these elements during magmatic differentiation. It was stated previously that titanium endeavors to become strongly enriched in the early products of crystallization and that the content of titanium may be high enough to characterize the chemistry of the early-separated oxide minerals. The content of zirconium, on the contrary, is low in the early crystallates, but during the main stage of crystallization this metal shows a tendency to become enriched in the last rocks to crystallize, viz., granites. In co-ordination zirconium (as well as hafnium) resembles manganese, but, because of its high valence, its *E*-value is high (Wickman, 1943). The absence of noteworthy amounts of zirconium in the early crystallates is partly due to the fact that its original concentration in the rock melt is low and partly to the circumstance that the Zr^{4+} ion is not readily incorporated in mineral structures, even though its

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E-value is high. The reasons are similar to those valid for the rare-earth metals (chap. 18).

The averages calculated by Daly (1933) for the chemical composition of the most important classes of igneous rocks do not include any values for ZrO_2 , but Hevesy and Wüstrlin (1934a) give the averages reproduced in Table 21.3.

In calc-alkalic rocks the concentration of zirconium does not continue after the pegmatitic stages are reached; zircon is not a characteristic constituent of granite pegmatites. The nepheline syenite pegmatites, on the other hand, often contain relatively plentiful zircon and the complex zirconium silicates.

TABLE 21.3
CONTENT OF ZIRCONIUM IN CALC-ALKALIC IGNEOUS ROCKS

Rock	Zr (g/ton)
Peridotites, eclogites, dunites	60
Gabbros	140
Diorites	280
Granites	460

CYCLE OF ZIRCONIUM

The conduct of titanium and zirconium during the minor cycle reveals the presence of notable differences, just as does their behavior during magmatic differentiation. This fact is chiefly due to the differences in the manner of occurrence of the two elements in rocks. As was stated previously, most zirconium in igneous rocks is contained in zircon, a mineral which is very stable against mechanical and chemical weathering. Therefore, zircon remains largely in the residates, which usually contain considerably more zirconium than do the hydrolyzates. However, zircon also goes gradually into solution, but the zirconates formed are less stable than the corresponding titanium compounds. Therefore, zirconium is rather readily removed from solution by hydrolysis and does not form secondary minerals. Any zirconium present in the weathering solutions will consequently become precipitated in the hydrolyzate sediments by adsorption. Yet this proportion is relatively small because of the low solubility of zircon, the most important zirconium mineral. The content of zirconium in sediments and their derivatives is lower, the more hydrolyzate material is incorporated in these rocks.

Very few determinations are available to show the content of zirconium in sediments. Hevesy and Wüstrlin (1934) report 500–900

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g./ton Zr in bauxite, 120 g./ton in shales and phyllites, and 140 g./ton in red clay.

In mineral waters the presence of zirconium is evidently caused by stable zirconium complexes (see chap. 6).

ZIRCONIUM ORES

Zircon and baddeleyite are the only important ore minerals of zirconium. They form placers of notable dimensions. The largest amount of zircon comes from Australia, followed by India and Brazil. The baddeleyite ores of Brazil contain 71–93 per cent ZrO_2 and 0.5–1.2 per cent HfO_2 . Nepheline-bearing rocks of the Poços de Caldas Plateau in Brazil contain huge quantities of zircon which is mined as a zirconium ore. These rocks and the zircon placers derived therefrom are claimed to be the greatest zirconium ores so far found. Sometimes the nepheline syenites may contain enough eudialite to make feasible its use as a technical source of zirconium.

HAFNIUM

Hafnium resembles zirconium very closely in its chemical properties and ionic size and always accompanies zirconium in Nature. As a matter of fact, no separation of hafnium from zirconium is known to take place in Nature. No independent hafnium minerals are known, and the content of hafnium in minerals never exceeds that of zirconium. The remarkable association of hafnium and zirconium is partly caused by the abundance relationships of these metals. The abundance ratio Zr:Hf is 48.9, whereas the ratio Cb:Ta is 11.4. Partly because of this lower ratio, columbium and tantalum, contrary to zirconium and hafnium, are actually separated from each other in Nature (see chap. 26). Hafnium and zirconium afford, perhaps, the most convincing example of the effect of the lanthanide contraction on the manner of occurrence of the heaviest atoms of the Periodic System in Nature. The radius of Zr^{4+} is 0.87 kX and that of Hf^{4+} is 0.86 kX. Like zirconium, hafnium is also always quadrivalent in the minerals. Zirconium and hafnium form a pronouncedly coherent pair of elements, perhaps the best example of such pairs. Where zirconium does not occur, hafnium is absent as well. All this shows that zirconium is a very powerful protective element (*Schutzelement*) of hafnium. No hafnium has been found in titanium and thorium minerals. It is a constituent exclusively of zirconium minerals.

Hevesy (1925) has shown that all zirconium minerals and the zirconium salts made therefrom regularly contain hafnium and that

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their hafnium content varies within rather narrow limits. The $\text{HfO}_2:\text{ZrO}_2$ ratio varies from 0.007 (fava) to 0.5 (thortveitite). The average HfO_2 content of baddeleyite, ZrO_2 , and zircon, $\text{Zr}[\text{SiO}_4]$, is 1 per cent. The highest HfO_2 content in minerals so far investigated is presented in Table 21.4, which is based on information given by Hevesy (1925), Hevesy and Wüerstlin (1928), and Lee (1928). The values show that the highest hafnium contents occur in certain altered hydrous zircons, called alvite, cyrtolite, malacon, and naëgite. The complex zirconium silicates found in many alkalic rocks usually contain much less hafnium. The content of hafnium in minerals of alkalic rocks in general seems to be somewhat lower than in those of calc-alkalic rocks, particularly granites. Thus, for instance, the zircons found in various nepheline syenites are always a little lower in hafnium than are the zircons of granites, the $\text{HfO}_2:\text{ZrO}_2$ ratios being 0.015 and 0.04, respectively.

TABLE 21.4
MAXIMUM CONTENT OF HAFNIUM IN ZIRCONIUM MINERALS

Mineral	HfO_2 Per Cent (Max.)
Zircon	6
Naëgite	7
Malacon	4
Cyrtolite	>10
Alvite	15
Baddeleyite	1.2
Thortveitite	1.1

The average hafnium content of zirconium is about 2 per cent (Hevesy and Wüerstlin, 1928).

Often the minerals with a high Hf:Zr ratio are more strongly radioactive than are the zircons and zirconium silicates with a lower content of hafnium. This is due to the concentration of uranium and thorium in the mother-liquors of granitic magmas, in which the enrichment of hafnium in respect to zirconium also takes place.

According to Hevesy and Wüerstlin (1928), hafnium also preferentially accompanies scandium and the yttrium-earth metals in minerals. Consequently, minerals with a high Hf:Zr ratio always contain much yttrium earths and usually scandium as well, e.g., cyrtolite, thortveitite, and thalenite. Likewise, the Hf:Zr ratio is high in scandium-bearing wolframites.

As in igneous rocks, hafnium accompanies zircon closely during all stages of the minor cycle, and no separation takes place at all.

Zircon is the most important source of hafnium.

TITANIUM, ZIRCONIUM, HAFNIUM

BIOGEOCHEMISTRY OF TITANIUM, ZIRCONIUM, AND HAFNIUM

Titanium is reportedly a microconstituent of plants and animals. However, often the analyses have been carried out by spectrochemical means, and it is believed that the impure carbon electrodes used have caused contamination. Therefore, no reliable information is at hand concerning the biological role of titanium. According to Mitchell (1944), the titanium content of soil is 1,000 g./ton and up. The content of titanium in plants seems to depend on its content in soil, and titanium would therefore seem a typical ballast element. Titanium is present in some marine animals.

Zirconium is present in soil in a content varying from 50 to 1,000 g./ton (Mitchell, 1944). It is taken up by the plants, but its biological role, if any, seems still to be unknown.

Nothing seems to be known about the biological importance of hafnium, and there is no information showing its content in organisms.

THORIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

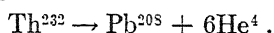
THORIUM was previously included in the group of the Periodic System in which titanium, zirconium, and hafnium are found. Thorium is always quadrivalent in its compounds. Its manner of occurrence in Nature resembles that of zirconium and hafnium in certain respects, although it also has features uncharacteristic of these elements. Along with the geochemical kinship between thorium and the three above-mentioned elements, there is also marked similarity between thorium, yttrium, and the lanthanides and between thorium and uranium. Therefore, thorium occupies, geochemically, an intermediate position between the rare-earth metals, zirconium (and hafnium), and uranium. Recent nuclear studies have resulted in the establishment of another group of rare-earth elements, called the actinides. Thorium, protactinium, uranium, and the transuranium elements are incorporated in this group (see chap. 18).

The following abundance values are considered most reliable for thorium in the metal phase of meteorites (Arrol, Jacobi, and Paneth, 1942), silicate meteorites (Noddack and Noddack, 1930), and igneous rocks (Goldschmidt, 1937*b*):

	Th (g ton)
Iron meteorites	0.04
Silicate meteorites	2-4.4
Igneous rocks	11.5

These values emphasize the strongly lithophile character of thorium. It is conspicuously concentrated in the lithosphere, particularly in the uppermost parts of this geosphere.

Thorium is radioactive, with a half-life of $1.389 \cdot 10^{10}$ years and heads a family of radioactive elements. An isotope of lead, Pb^{208} (ThD), is formed, after the successive emission of 6 α - and 4 β -particles, by the disintegration of the single isotope of thorium, Th^{232} , which occurs in Nature:



Thus lead accumulates in thorium-bearing minerals.

THORIUM IN IGNEOUS ROCKS

The igneous rocks contain the average quantities of thorium shown in Table 22.1. These values show that thorium is strongly concentrated in the acidic rocks during the magmatic differentiation. In this respect it resembles zirconium, yttrium and the lanthanides, and uranium but differs from titanium. After the close of the main stage of crystallization the concentration of thorium still continues during the pegmatitic stage. This is explained by its high valency, notwithstanding the magnitude of its E -value and the fact that the Th^{4+} ion resembles Ca^{2+} in co-ordination (chap. 5).

The average Th:U ratio in igneous rocks is 3.2 (Keevil, 1944). Senftle and Keevil (1947) found the value 3.4 for this ratio in acidic,

TABLE 22.1
THORIUM CONTENT OF IGNEOUS ROCKS

Rock	Th (g. ton ⁻¹)
Basalt (Evans and Goodman, 1941)	5 0
Diabase (Evans and Goodman, 1941)	2 0
Granite (Senftle and Keevil, 1947)	13 45
Basic igneous rocks, weighted average (Evans and Goodman, 1941)	3 9
Intermediate igneous rocks (Senftle and Keevil, 1947) . .	9 97
Acidic igneous rocks, weighted average (Evans and Goodman, 1941)	13 0

and 4.0 in intermediate, igneous rocks. They suggest that acidic magmas, although more radioactive than the intermediate ones, retain more uranium than thorium.

Only two independent thorium minerals are known, viz., thorianite $(\text{Th,U})\text{O}_2$, and thorite (orangite), $\text{Th}[\text{SiO}_4]$, which are rare constituents of pegmatites. Thorite is isomorphic with zircon, $\text{Zr}[\text{SiO}_4]$, and it is evident that a large part of thorium in the upper lithosphere is incorporated in the zircon structure. The ionic sizes of thorium and zirconium are not too unlike ($r_{\text{Th}^{4+}} = 1.10$ kX; $r_{\text{Zr}^{4+}} = 0.87$ kX), and therefore thorium is able to enter the zircon structure, in which it replaces, at least at the temperature of crystallization, zirconium diadochically. Thorium is also camouflaged in other zirconium minerals. However, according to Hutton (1947), zircon in some granites is not radioactive, whereas monazite and xenotime are strongly so. Consequently, available thorium and uranium, owing to their ionic dimensions, seem to prefer the rare-earth minerals, whereas the zircon structure allows only a very limited degree of substitution.

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Thorianite illustrates the close geochemical relationships between thorium and uranium. Thorium dioxide, as thorianite, has a structure of the calcium fluoride type, and it forms the end-member in the artificially produced series in which uranium dioxide, UO_2 , is found as the uranium end-member. The complete isomorphic series has not been found in Nature. Uraninite, if its structure is not decomposed, occurs as crystals which are isotypic with thorianite. However, all natural members of this series, as well as uraninite and thorianite, are chemically rather complicated, and the formulas given above are much idealized. A mixture containing relatively much thorium is called bröggerite, $(\text{U,Th})\text{O}_2$, and the other varieties often bear local names. Thorium is found to accompany uranium also in many other uraniferous pegmatite minerals.

The Zr-Th and U-Th diadochy characterizes the geochemistry of thorium. Another remarkable feature is the occurrence of thorium together with the rare-earth metals. Notwithstanding the fact that thorium does not belong to the same group in the Periodic System as the lanthanides, there is a close chemical similarity between the rare-earth metals and thorium; and thorium is often considered a member of the rare-earth group. It is captured in the structures of the lanthanide minerals because the ionic sizes of the elements in question are very much alike. The rule is that where the cerium earths preponderate, i.e., usually in syenite and nepheline syenite pegmatites, thorium is regularly found to be present. Monazite and allanite as a rule contain considerable quantities of thorium (5–10 per cent ThO_2 in monazite). This manner of occurrence is quantitatively of as high importance in the geochemistry of thorium as is the presence of thorium in zircon. In monazite, Th^{4+} is captured by the trivalent lanthanides, and simultaneously $[\text{SiO}_4]^{4-}$ substitutes for $[\text{PO}_4]^{3-}$.

CYCLE OF THORIUM

During the minor cycle thorium follows the lanthanides rather closely. Monazite, the most important rare-earth mineral, is concentrated in the resistates and may form relatively rich layers in sands and gravels if its amount in the weathering rocks was formerly high. Such monazite sands, derived from granites and gneisses, are the principal sources of thorium. The most important deposits are found in Travancore, India, which is reported to yield 75 per cent of the world's total thorium supply. Thorianite (with about 80 per cent

ThO_2) and thorite (66–70 per cent ThO_2) are less important sources of thorium.

Part of thorium is brought into solution during the weathering but is easily hydrolyzed and accumulates in the hydrolyzates, which are notably rich in thorium. The average thorium content of sedimentary rocks is given in Table 22.2.

The igneous rocks contain, on an average, approximately three times as much thorium as uranium. In sea water, on the contrary, the

TABLE 22.2
THORIUM IN SEDIMENTARY ROCKS

Rock	Th (g ton)
Rocks of arenaceous origin (Joly, 1910).....	5.4
Rocks of argillaceous origin (Joly, 1910).....	12
Shales (Minami, 1935a).....	10.1
Limestones (Evans and Goodman, 1941).....	1.1

content of uranium is at least three times as high as that of thorium (see Table 6.17). The higher abundance of uranium in the oceans is explained by Pettersson (1939) as being due to the precipitation of thorium with hydroxides of iron and manganese, whereby it is deposited partly in the hydrolyzates and partly in the oxidate sediments. The Th:U ratio attains high values in these sediments because uranium is not precipitated in such surroundings. A little thorium is also present in limestones.

Very little information seems to be available on the occurrence of thorium in the biosphere. According to Mitchell (1944), the thorium content of soil may be as high as 0.1 per cent Th. In such cases thorium might perhaps be enriched in biochemical processes. It is known that thorium, in small concentrations, stimulates the growth of some plants.

NITROGEN

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

NITROGEN is one of the most abundant elements in celestial sources, being a common constituent of the atmospheres of the stars, the Sun, and the planets. Nitrogen lines are abundant in the spectra of the hotter stars and of the nebulae. The solar atmosphere contains the molecules and radicals N_2 , ON, CN, NH, and SiN. Ammonia, NH_3 , occurs in the atmospheres of the giant planets. The silicate meteorites are rather poor in nitrogen, but the nitrogen content of igneous rocks is very much higher than was previously assumed. The abundance values are given in the accompanying tabulation. According to its content in igneous rocks, nitrogen is actually

Material	N (g/ton)
Chondrites (Noddack and Noddack, 1934)	0.9
Igneous rocks (Lord Rayleigh, 1939)	46.3

one of the more abundant elements in the upper lithosphere.

The classification of the elements presented in Table 4.3 shows that nitrogen is geochemically pronouncedly atmophile. The bulk of the atmosphere, or 755 g per cm^2 of the Earth's surface, consists of nitrogen (chap. 7). In addition, nitrogen oxides and ammonia occur as regular constituents of the atmosphere: Adel (1939) has identified N_2O and N_2O_5 as permanent constituents therein. They are probably formed in photochemical and, partly, biochemical reactions. The formation of NO_2 in the atmosphere is probably caused by electrical discharges.

The atmophile properties of nitrogen differ from those of oxygen. Oxygen is chemically active and combines with most other elements to form oxides, being thus removed from the atmosphere. Therefore, the free oxygen of the atmosphere is more or less unstable, and this element is chiefly lithophile. As a matter of fact, the bulk of the lithosphere consists of oxygen (see chap. 27). Nitrogen, on the other

hand, is chemically rather inert and consequently does not play an important part in chemical processes taking place on the Earth's surface but remains largely in the atmosphere. Therefore, the atmophile character of nitrogen is more pronounced than that of oxygen.

Like hydrogen, nitrogen is a characteristic constituent of volcanic emanations. It was previously believed that the nitrogen in volcanic gases is of atmospheric origin, but now it is held that the bulk of molecular nitrogen in these gases is purely magmatic. It seems to be certain that the nitrogen content of the atmosphere has increased during the geological history of the Earth as a result of volcanic activity.

Nitrogen is of high importance in biochemical processes. The values presented in Table 8.1 show that the nitrogen content of organisms varies from 1 to 60 per cent. Nitrogen is a decidedly biophile element. Owing to the small mass of the biosphere, the amount of nitrogen found therein is small and thus may usually be neglected in geochemical calculations. Likewise, the amount of nitrogen in sea water and in some evaporate sediments may generally be left out of calculations.

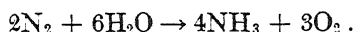
Small amounts of nitrogen are also present in organic compounds in sediments and sedimentary rocks. Goldschmidt (1937*b*) estimates the quantity of nitrogen found therein as about 3 per cent of the organic carbon found in these rocks. Because the amount of carbon is about $500 \text{ g}\cdot\text{cm}^{-2}$, the quantity of nitrogen amounts to approximately $15 \text{ g}\cdot\text{cm}^{-2}$. Added to the amount of nitrogen found in the atmosphere, this gives $770 \text{ g}\cdot\text{cm}^{-2}$, which is the total quantity of nitrogen liberated in the terrestrial degassing products. Assuming the average nitrogen content of igneous rocks to be 0.00463 per cent by weight, the $160 \text{ kg}\cdot\text{cm}^{-2}$ of igneous rocks weathered during the geological history of the Earth would have produced a total of $7.4 \text{ g}\cdot\text{cm}^{-2}$ nitrogen, provided that all nitrogen liberated during the weathering finally escaped into the atmosphere. This amount is only about one one-hundredth of the total degassed nitrogen, and consequently it seems to be evident that much nitrogen is released directly into the atmosphere by volcanic activity. It might also be possible that some nitrogen now found in the atmosphere is primitive, being a remain of the protoatmosphere.

According to Hutchinson (1944), Goldschmidt's value ($15 \text{ g}\cdot\text{cm}^{-2}$) is probably too low. The average content of combined nitrogen in sediments is given by Hutchinson as 510 g/ton, of which 460 g/ton

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is fossil nitrogen, lost from the biosphere. Taking, according to Goldschmidt (1933a), the total amount of sediments as $170 \text{ kg} \cdot \text{cm}^{-2}$, these values give 87 and $78 \text{ g} \cdot \text{cm}^{-2}$, respectively. Compared with the amounts of fossil oxygen ($485\text{--}794 \text{ g} \cdot \text{cm}^{-2}$; chap. 27) and fossil carbon ($210 \text{ g} \cdot \text{cm}^{-2}$; chap. 19), the quantity of fossil nitrogen appears strikingly small.

Hutchinson (1944) has also called attention to the fact that 1.71 g oxygen are liberated for each gram of nitrogen fixed in the formation of ammonia, according to the reaction



Therefore, the fixation of the estimated $73 \text{ g} \cdot \text{cm}^{-2}$ of fossil nitrogen corresponds to the liberation of $125 \text{ g} \cdot \text{cm}^{-2}$ oxygen into the oxygen-carbon dioxide cycle. This is a little more than half the existing supply of oxygen ($230 \text{ g} \cdot \text{cm}^{-2}$) in the atmosphere (see chap. 7). However, some of the ammonia probably comes from juvenile sources, thus causing a corresponding decrease in the estimate. When the amount of oxygen liberated in the above-mentioned process ($125 \text{ g} \cdot \text{cm}^{-2}$) is added to the quantity consumed in the production of the total of $760 \text{ g} \cdot \text{cm}^{-2}$ CO_2 in the carbon cycle ($550 \text{ g} \cdot \text{cm}^{-2}$; see chap. 19) and when the sum ($675 \text{ g} \cdot \text{cm}^{-2}$) is compared with the amount of fossil oxygen ($485\text{--}794 \text{ g} \cdot \text{cm}^{-2}$; chap. 27), the higher of the two estimates is seen to correspond more closely to the known facts.

NITROGEN IN IGNEOUS ROCKS

In the upper lithosphere nitrogen seems to be oxyphile, but no detailed information is so far available on its manner of occurrence. The igneous rocks have not been reported to contain any independent nitrogen minerals which should indisputably have been formed by direct crystallization of magma. The iron nitride siderazot (silvestrite), Fe_3N_2 , is found as a thin coating on some lavas, but it may be of secondary origin, formed in the reaction between hot lavas and atmospheric nitrogen. Volcanic emanations produce a number of ammonium salts, e.g., sal ammoniac, NH_4Cl . The ammonium compounds were believed to result from the decomposition of boron nitride by water vapor. Other possibilities of their formation were suggested in addition. As early as 1847, the German chemist, Robert Wilhelm Bunsen, suggested that the destructive distillation of organic matter is the source of the ammonium compounds in certain volcanic regions. Zies (1929), when discussing the origin of ammoni-

um minerals in the Valley of Ten Thousand Smokes in Alaska, adhered to Bunsen's explanation, for which certain geological features of the Katmai area seemed to afford further support. However, Berbey (1947) showed that the ammonium salts produced by the volcanoes may originate in the reaction between the nitrogen of the air and the hydrogen of water vapor under the catalytic action of the ferromagnesian minerals of the lavas.

According to Lord Rayleigh (1939), igneous rocks contain, on an average, 0.00463 per cent N. This nitrogen appears to be mainly in chemical combination, perhaps as ammoniacal nitrogen. At least, not all nitrogen is held in the structures of minerals, unlike the probable manner of occurrence of the rare gases (chap. 45). Nitrate nitrogen in rocks, if any, can be only a small part of the whole.

The possibility of the diadochic substitution of K^+ (radius 1.33 kX) by $[NH_4]^+$ (radius 1.43 kX) might offer a possibility of explaining the manner of occurrence of nitrogen in rocks, but this problem has so far attracted no attention.

The nitrogen content of igneous rocks is remarkably constant, as the figures given in the accompanying tabulation show (Lord Ray-

Rock	N (ml/g)
Dunite, average	0.045
Gabbro	0.037
Granite, average.	0.037

leigh, 1939).

The composition of gases obtained by the heating of igneous rocks is illustrated by three analyses made by W. A. Tilden in 1896, quoted from Clarke (1924) and reproduced in Table 23.1. Although the analyses in this table do not represent the composition of all gases evolved from igneous rocks, they show that hydrogen and carbon dioxide predominate among the gases and that a notable content of nitrogen is also present.

CYCLE OF NITROGEN

The nitrogen compounds are liberated from rocks during the weathering. According to Clarke (1924), the dissolved solids in river waters contain, on an average, 0.90 per cent nitrate nitrogen (see Table 6.7). At least a part of this nitrogen is of organic origin, being liberated during the decay and subsequent oxidation of organic matter. Ammonium salts of inorganic origin are produced by volcanic activity and brought down in precipitation. Organic nitrogen is de-

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rived from organic matter and its products of decomposition. Nitrogen fixed in the atmosphere by electrical discharges, by photochemical reactions, and in the trail of the meteors is also brought down by precipitation, as are the nitrogen compounds derived from industrial contamination. All this nitrogen is present as nitrous acid, HNO_2 , nitric acid, HNO_3 , and their salts. Cyclical nitrogen is also present in rain water, viz., cyclical ammonia, cyclical nitrate, and cyclical nitrite. Such nitrate comes from the soil and the ocean. The organic nitrogen in rain is probably all cyclical.

Notable amounts of nitrogen are thus carried to the sea, but this amount is small if compared with the total quantity stored in sea water. In the sea, nitrogen is absorbed by plants and built up into

TABLE 23.1
COMPOSITION OF GASES EVOLVED FROM IGNEOUS ROCKS

Rock	H ₂	N ₂	CO ₂	CO	CH ₄	TOTAL
	Per Cent by Volume					
Basalt	36 15	1 61	32 08	20 08	10 00	99 92
Gabbro	88 42	1 90	5 50	2 16	2 03	100 01
Granite.. . . .	61 68	5 13	23 60	6 45	3.02	99 88

their cell substance. Therefore, the nitrogen content of sea water remains low, and particularly the surface layers, which are rich in plankton organisms, are depleted in nitrogen. According to Table 6.17, the content of the various compounds of nitrogen in sea water is shown in the accompanying tabulation.

Nitrogen Compound	Content (g/ton)
Nitrogen as nitrate.....	0.001 -0.7
Nitrogen as organic nitrogen.....	0.03 -0.2
Nitrogen as nitrite.....	0.0001-0.05
Nitrogen as ammonia.....	>0.005 -0.05

All nitrogen compounds show a wide range of concentration values from place to place, because there occur seasonal changes in the upper layers. Sea water also contains particulate nitrogenous material of organic origin, and organic nitrogen compounds are found in marine organisms. The values recorded above show that the bulk of nitrogen in ionic solution consists of nitrate nitrogen. This is always

the case in the deep waters, but, in surface layers of the ocean, nitrate is the most abundant inorganic form of nitrogen only preceding the vegetative season.

Sea water also contains considerable amounts of dissolved gases, particularly in the upper layers. The abundance ratio between dissolved nitrogen and oxygen in sea water differs from the corresponding ratio in the air. According to Table 6.18, the concentration of dissolved nitrogen in sea water varies from 8.4 to 14.5 ml/l. Nitrogen is notably impoverished in the gases dissolved in sea water, as compared to its content in the atmosphere. It is possible that a certain amount of fixed nitrogen in sea water is liberated and returns to the atmosphere as free nitrogen; but this amount is necessarily small, like that of dissolved nitrogen utilized by plants.

During the formation of sediments, nitrogen in the form of organic compounds is incorporated in the rocks deposited. Sediments containing organic matter thus become enriched in nitrogen, but the fate of this element during diagenesis and metamorphism is still unknown.

Ammonium salts, nitrates, and nitrites are all readily soluble, and their content in sea water is low. Therefore, marine salt deposits do not contain notable amounts of these salts. Thus, e.g., no ammonium salts occur as characteristic constituents in the Stassfurt salt beds in Germany. Evaporate sediments containing nitrates are, however, found in arid regions; they are continental formations, ultimately deposited from ground waters, though their origin is still a matter of controversy. The greatest nitrate deposits occur in South America in the desert regions of northern Chile. The composition of the Chilean nitrate beds (caliche) is variable. They consist chiefly of nitrates, chlorides, sulfates, borates, perchlorates, and iodates of sodium, potassium, calcium, and magnesium. The presence of perchlorates, iodates, and some chromates and selenates in these deposits affords proof of a very high redox potential. In fact, their redox potential is the highest so far recorded on the Earth. Niter (nitrokalite), KNO_3 , and nitratite (nitronatrite), NaNO_3 , are the most abundant nitrates in caliche. However, halite and gypsum are more abundant constituents than the nitrates. Some deposits contain 50 per cent nitrates or still more, but they are rare. The nitrate deposits form an important source of nitrogen, but increasing amounts of nitrogen compounds are now made from the atmospheric nitrogen by electrochemical processes.

NITROGEN AND ITS CYCLE IN THE BIOSPHERE

Nitrogen occurs in all living organisms, usually as a constituent of proteins. In addition, most recent and fossil substances of organic origin contain nitrogen. Some inorganic compounds of nitrogen are found in biochemical systems, viz., ammonia, NH_3 ; hydroxylamine, NH_2OH ; nitrous acid, HNO_2 ; nitric acid, HNO_3 ; and the salts (nitrites and nitrates) of the two acids. Simple organic compounds of nitrogen of biological importance are known, such as hydrocyanic acid, HCN ; urea, $\text{CO}(\text{NH}_2)_2$; and a number of amines, amino acids, etc. The complex organic compounds of nitrogen include purines, porphyrins, proteins, and many others.

The geochemical cycle of nitrogen is intimately connected with the biosphere, and its cycle in the biosphere forms an important part of the cycle as a whole. The biophile character of nitrogen is rather pronounced, and its cycle in the biosphere is its most prominent geochemical feature. The cycle of nitrogen in the biosphere and the adjoining geochemical spheres is presented in Figure 23.1, which is mainly based on the surveys presented by Gilson (1937), Eskola (1939), and Fearon (1947). It should be noted that the French chemist, Jean Baptiste André Dumas (1800–1884) was the first to present, in 1841, a general scheme of the cycles of nitrogen and carbon.

Plants use nitrogen as a nutrient to form the complex protein and other molecules, which, in turn, form the nitrogen source of the animals. In order to be able to participate in biochemical processes, the atmospheric free nitrogen must first be converted into nitrate. The nitrogen fixation is partly a result of industrial activity; but by far the greatest part of nitrogen is fixed by micro-organisms living in the root nodules of leguminous plants, by soil organisms, both aerobes and anaerobes, and by some blue-green algae. A small part of nitrate nitrogen is derived from the atmosphere, where it is produced by electrical and photochemical processes. Nitrogen-fixing nodules are also found in some other plants, e.g., in the leaves of rubiaceous plants and in the roots of alder. Micro-organisms capable of assimilating nitrogen occur, in addition, in both fresh and salt water. The following metals are necessary for the biological fixation of nitrogen in soil: calcium, magnesium, molybdenum, and iron; calcium may be replaced by strontium and molybdenum by vanadium.

In herbivorous animals the plant proteins are decomposed and re-synthesized into animal proteins. The higher animals excrete the

Nitrogen-fixing bacteria

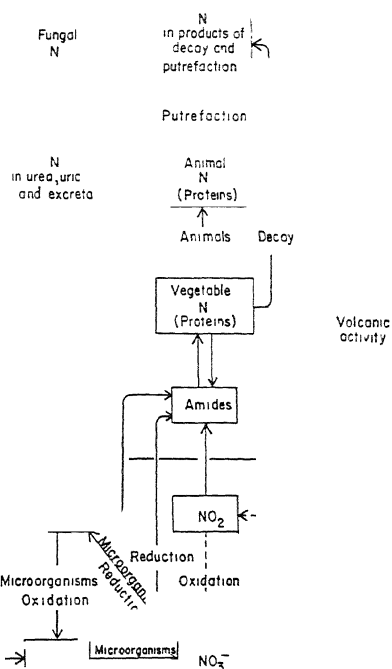
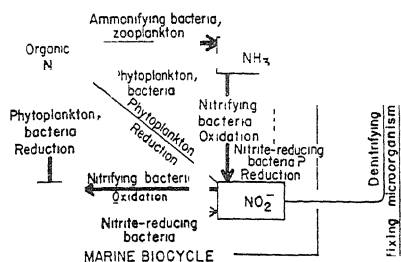


FIG. 23.1.—The cycle of nitrogen, chiefly in the biosphere

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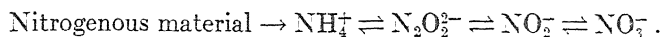
waste nitrogen as urea. This compound is rapidly attacked by micro-organisms, which convert it into ammonia. In this form nitrogen re-enters the circulation. Birds and reptiles excrete nitrogen as uric acid, which is more stable and more insoluble than urea and may therefore accumulate under proper conditions. If such is the case, nitrogen is temporarily withdrawn from the cycle, e.g., in the guano deposits of the Pacific islands which consist chiefly of the excrements of seafowl (see chap. 24).

During the decay of plants and animals after death, their complex organic nitrogenous compounds are decomposed by bacteria. This decomposition is mainly due to proteolytic bacteria, which first produce amino acids, then ammonia, nitrites, and, finally, nitrates. A part of the ammonia, if liberated, may escape into the atmosphere or dissolve in water. Bacteria are also known which are capable of splitting off the NH_2 group of the amino acids (ammonification). The ammonia is usually oxidized (nitrification), first into nitrites, then into nitrates by other bacteria, and thus it re-enters the cycle. The nitrates, on the other hand, may be reduced by nitrate-reducing ($\text{NO}_3^- \rightarrow \text{NO}_2^-$) and denitrifying ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2$) bacteria. In the second case nitrogen is lost from the organic cycle into the atmosphere. The wealth of bacteria connected with the cycle of nitrogen also includes those that are capable of reducing nitrates to ammonia and other species which convert nitrites and nitrates into organic substances and still others able to fix atmospheric nitrogen to produce organic substances.

In the marine biocycle the migration of nitrogen is rather complicated. The amount of nitrate, like that of phosphate, is controlled in the sea by the consumption by phytoplankton and the regeneration from its remains. Marine animals excrete nitrogen-bearing substances into sea water, mainly ammonia. The deep ocean waters contain a huge supply of nitrate, which is the most stable form of nitrogen. Because nitrate is the most abundant form of inorganic nitrogen in the sea, most organisms are able to obtain their principal supply of nitrogen from nitrate, but some may also utilize nitrites, ammonium salts, and simple organic compounds. The abundance of nitrate in deep ocean water emphasizes the role of the bottom as the principal site of the nitrification processes.

As on land, so also in the sea the role of bacteria in the transformation of organic nitrogen into inorganic forms and in the reactions be-

tween ammonia, nitrite, and nitrate is very important. It is probable that the reactions take place according to the following scheme:



Much energy is released in the formation of ammonium salts and of hyponitrite and nitrite.

According to Hutchinson (1944), the ocean, contrary to the case of carbon dioxide, is not the general reservoir and stabilizing mechanism of ammonia in the cycle of nitrogen.

Chitin, a very stable and insoluble nitrogen-bearing carbohydrate, is found in the exoskeletons of insects and crustaceans and in the supporting tissue of fungi. In the form of chitin, nitrogen is at least temporarily withdrawn from the cycle. The total rate of nitrogen fixation for the whole Earth can hardly be less than $0.0034\text{--}0.017 \text{ mg}\cdot\text{cm}^{-2}$ annually (Hutchinson, 1944), and consequently the present-day supply of $755 \text{ g}\cdot\text{cm}^{-2}$ of atmospheric nitrogen would last from $44\cdot 10^6$ to $220\cdot 10^6$ years. Hutchinson estimates that if no chitin-splitting organisms had developed and no inorganic decomposition of nitrogen-bearing organic substances had taken place, the current rate of chitin production would have exhausted the nitrogen supply of the atmosphere in $41\cdot 10^6$ years, provided that adequate nitrogen fixation had occurred.

Two nitrogen isotopes exist, N^{14} and N^{15} , the former being by far the more abundant. Some amino acids are known to contain N^{15} in excess of atmospheric nitrogen, but the cause of this change in the isotopic abundance ratio is still unknown.

PHOSPHORUS

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE abundance of phosphorus in the meteorite phases and in igneous rocks is presented in Table 24.1. Phosphorus has also been detected and quantitatively determined in the solar atmosphere (see chap. 2).

Phosphorus is one of the most abundant trace elements of the upper lithosphere. However, its abundance values show clearly that it does not belong among the typically lithophile elements. It is evident that phosphorus, unlike many other elements, does not show any well-determined behavior as far as its distribution among the sili-

TABLE 24.1
ABUNDANCE OF PHOSPHORUS

Material	P (g/ton)
Metal phase of meteorites (Goldschmidt, 1937 <i>b</i>)	1,800
Sulfide phase of meteorites (Goldschmidt, 1937 <i>b</i>)	3,000
Silicate phase of meteorites (Goldschmidt, 1937 <i>b</i>)	700
Igneous rocks (Conway, 1945)	1,200

cate, sulfide, and metal phases in physicochemical systems is concerned. Thus, e.g., the metal phase of the meteorites contains only 2.6 times as much phosphorus as does the silicate phase.

Phosphorus and nitrogen belong to the same subgroup of the Periodic System. Phosphorus, like nitrogen, may occur as a trivalent negative, and as a quinquevalent positive, ion. In the metal phase of the meteorites and in the troilite nodules, phosphorus forms the phosphide schreibersite, $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$. The troilite nodules may contain as much as 1.16 per cent P (Goldschmidt, 1935). However, the stability of schreibersite depends on the redox potential of the system, and only in the metal and sulfide phases of the meteorites with their very low redox potential, as compared with terrestrial igneous rocks, may schreibersite be stable. The stony meteorites and particularly the igneous rocks of the upper lithosphere are rich in oxygen,

and phosphorus is present therein only as quinquepositive ions, which form a part of the orthophosphate ion, $[\text{PO}_4]^{3-}$.

The abundance values of phosphorus show that this element is siderophile, with a pronounced lithophile tendency. In spite of its high content in the troilite nodules, phosphorus hardly possesses any strong chalcophile features.

PHOSPHORUS IN IGNEOUS ROCKS

In the upper lithosphere, phosphorus is oxyphile.

Phosphorus, titanium, and manganese are the trace elements usually determined during the course of a chemical rock analysis made for petrological purposes. Therefore, numerous analyses are available, showing the content of phosphorus in igneous rocks. The investigation of the geochemistry of phosphorus in these rocks is also greatly facilitated by the fact that, even though present only in small quantities, it tends to form an independent mineral, viz., apatite, $\text{Ca}_5[(\text{F}, \text{Cl}, \text{OH}) | (\text{PO}_4)_3]$. This mineral, with a P_2O_5 content ranging from 41 to 42.5 per cent, is one of the most common accessory constituents of igneous rocks, and it is evident that by far the greatest part—perhaps as much as 95 per cent or more—of the phosphorus of igneous rocks is present in apatite.

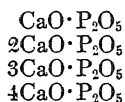
The fact that phosphorus follows very closely the course of titanium during the magmatic differentiation was pointed out by Vogt (1931). The average chemical composition of the calc-alkalic igneous rocks, calculated by Daly (1933; see Table 5.32), reveals that phosphorus, like titanium, shows a pronounced tendency to become concentrated during the earliest steps of the main stage of crystallization. In alkalic rocks—for example, in syenite, nepheline syenite, and especially basic alkalic rocks—phosphorus may even occur among the main constituents. In the early-separated silicates, such as dunite, phosphorus and titanium are relatively rare. On the other hand, the phosphorus content of magmatic sulfides is rather high: 2,500 g/ton, according to Noddack and Noddack (1931a). The manner of occurrence of phosphorus in sulfide minerals seems to be unknown.

As was emphasized by Vogt (1931), phosphorus and titanium afford a good example of a pair of elements which accompany each other in igneous rocks in spite of the great difference in their chemical behavior. Unlike the pairs zirconium-hafnium, nickel-cobalt, and zinc-cadmium, which are geochemically coherent because of their

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position in the Periodic System, the only common feature of titanium and phosphorus is the tendency of their most abundant minerals—ilmenite, sphene, and apatite—to become separated from the magma under similar circumstances. Consequently, these elements usually occur in the same rock. It is evident that the geochemical affiliation of phosphorus and titanium is coincidental and not based on any chemical similarity.

A feature characterizing phosphorus geochemically is its property of forming numerous phosphate minerals with a number of cations; such minerals occur in pegmatites, in pneumatolytic, and especially in hydrothermal, rocks. The phosphate minerals, however, are usually mineralogical curiosities and have but little importance in the geochemistry of phosphorus. The bulk of phosphorus is found in apatite. As to other calcium phosphates, thermochemical studies on the system $\text{CaO-P}_2\text{O}_5$ carried out by G. Trömel in 1932 (according to Eitel, 1941) show that four different phosphates crystallize in this system, viz.,



The compound $3\text{CaO} \cdot \text{P}_2\text{O}_5$ or $\text{Ca}_3[\text{PO}_4]_2$ occurs as a rare constituent (whitlockite) in hydrothermal rocks.

Crystal chemical studies have revealed the presence of a separate anion as an essential constituent of the structure of apatite, along with the phosphate group. This anion consists usually of Cl, F (see chap. 44), OH, or CO_3 , and the apatites are accordingly called chlorapatites, fluorapatites, hydroxylapatites, and carbonate apatites. In chlorapatite, F is partly or totally replaced by Cl, and in oxyapatite (voelckerite), 2F is replaced by 1O. The most common magmatic apatite is a mixture: $\text{Ca}_5[(\text{F}, \text{Cl}, \text{OH})|(\text{PO}_4)_3]$. According to McConnell (1938), the pure carbonate apatite and oxyapatite, $\text{Ca}_{10}[\text{CO}_3|(\text{PO}_4)_6]$ and $\text{Ca}_{10}[\text{O}|(\text{PO}_4)_6]$, do not exist in Nature. The $[\text{PO}_4]$ group of apatite may be replaced by the following groups: $[\text{AsO}_4]$, $[\text{VO}_4]$, $[\text{SO}_4]$, and $[\text{SiO}_4]$, and Ca may be replaced by Na, K, Sr, TR, and Mn. According to Mitchell, Faust, Hendricks, and Reynolds (1943), hydroxylapatites are formed only by metamorphic processes in the presence of much water and with the simultaneous formation of other minerals rich in hydroxyl groups, e.g., talc and chlorite. In this case the fluorine of the apatite becomes replaced by hydroxyl.

In apatite and all other phosphate minerals the phosphorus-oxygen complex forms $[\text{PO}_4]$ tetrahedra which are structurally comparable with the $[\text{SO}_4]$ groups of the sulfates. It should be noticed that in phosphate minerals the $[\text{PO}_4]$ groups, unlike the $[\text{SiO}_4]$ tetrahedra of the silicates, are not linked together but are always present as separate groups.

Only a small proportion of all phosphorus occurs elsewhere than in the apatite in igneous rocks. This part forms, particularly during the last steps of the main stage of crystallization, a number of phosphate minerals, usually of rare and limited occurrence. They include the rare-earth phosphates monazite, $\text{Ce}[\text{PO}_4]$, with 26–30 per cent P_2O_5 , and xenotime, $\text{Y}[\text{PO}_4]$, which contains 29–35 per cent P_2O_5 . Monazite and xenotime are minor constituents of granites, particularly of granite pegmatites. In granite and nepheline syenite pegmatites, phosphorus forms, in addition, a number of lithium, beryllium, aluminum, and manganese phosphates, e.g., beryllonite, $\text{NaBe}[\text{PO}_4]$, which is isotypic with quartz; triphylite, $\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})[\text{PO}_4]$, isotypic with olivine; triplite, $(\text{Fe}^{2+}, \text{Mn}^{2+})_2[\text{F}|\text{PO}_4]$; and amblygonite, $\text{LiAl}[(\text{F}, \text{OH})|\text{PO}_4]$. Amblygonite is of importance as an ore of lithium. Its phosphorus content runs from 46 to 49 per cent P_2O_5 .

The huge nepheline syenite area in the central part of the Kola Peninsula in Russia affords an example of the existence of a residual magma very high in phosphorus. This magma intruded the surrounding rocks and formed vast bodies of apatite rock, comparable with intrusive bodies consisting of pegmatite.

Another manner of occurrence of phosphorus in minerals is its property of substituting for silicon in the silicon-oxygen framework of silicates, even in the independent $[\text{SiO}_4]$ tetrahedra. As much as approximately 25 per cent of the $[\text{SiO}_4]$ groups have been found to be replaced by $[\text{PO}_4]$ groups in some Japanese zircons, the Zr^{4+} being replaced by trivalent rare-earth metals in order to maintain the electrical neutrality of the structure. Mason and Berggren (1941) found up to 4.10 per cent P_2O_5 in a spessartite garnet, a part of the $[\text{SiO}_4]$ groups being replaced by $[\text{PO}_4]$ groups. The degree of replacement is probably regulated by the conditions prevailing during the time of formation of the mineral. The radii of Si^{4+} (0.39 kX) and of P^{5+} (0.35 kX) make a diadochic replacement plausible; and numerous artificial compounds, e.g., the silicophosphates of alkali and alkaline-earth metals, reveal the possibility of an unlimited replacement of Si^{4+} by P^{5+} . As emphasized by Mason and Berggren, phosphorus, in

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small amounts at least, may be much more common in silicate minerals than has been suspected. Detailed research in this field would be welcome.

PHOSPHORUS AND ITS CYCLE IN THE BIOSPHERE

The manner of occurrence of phosphorus in the biosphere reveals its distinctly biophile character. Phosphorus is an essential constituent of cytoplasm. All plants contain phosphorus, and the phosphate content of soil is one of the factors which limit the growth of plants. Phosphorus is an important constituent of bones, teeth, and many shells in animals. In mammals most of the phosphorus is incorporated in the skeleton. Higher organisms are usually richer in phosphorus than are the lower forms.

Salts of orthophosphoric acid occur in tissues and tissue fluids (anions H_2PO_4^- and HPO_4^{2-}) and in bones (anion PO_4^{3-}). Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, forms labile esters which are important in the energy transfer in many biochemical processes. Phosphorus is also a constituent of lipides and many proteins. Phosphates stabilize the pH of cell and tissue fluids.

Phosphorus circulates in the biosphere as phosphate. The cycle of phosphorus in the biosphere is an important part of its general geochemical cycle. Plants take up phosphorus from soil, as soluble phosphates, to synthesize phospholipides and other phosphoriferous compounds. In animals feeding upon plants these substances are transferred into tissue phosphates and phosphoproteins. The excess phosphorus is excreted as phosphate, in the higher animals chiefly by the kidney.

In the marine biocycle the migration of phosphorus is very similar to the cycle of nitrogen, but only one inorganic form, viz., the phosphate ion, is known to occur. The cycle is biologically activated and involves the alternation of organic and inorganic forms. Marine plants and animals extract phosphates from water for their structures and cytoplasm. Although soluble phosphates are the main source of phosphorus for the plants, it might be possible that phytoplankton organisms obtain a part of their phosphorus from dissolved organic phosphorus complexes. In any case, organic compounds form an intermediate stage in the regeneration of phosphorus. Owing to the action of scavengers and bacteria on the remains of the organisms, phosphorus re-enters sea water as soluble phosphate. The phosphate utilized by phytoplankton returns to the sea relatively completely.

A part of the phytoplankton phosphates is returned directly by herbivores and carnivores which excrete phosphate, and another part comes in the fecal pellets. Some phosphate is also regenerated indirectly during the decomposition of stable organic phosphorus compounds dissolved in sea water. The role of bacteria in the cycle is still unknown, but it is possible that some phosphorus is precipitated by bacteria, because some species are known to contain this element.

Some phosphorus escapes the cycle in the sea and is deposited in the accumulating sediments.

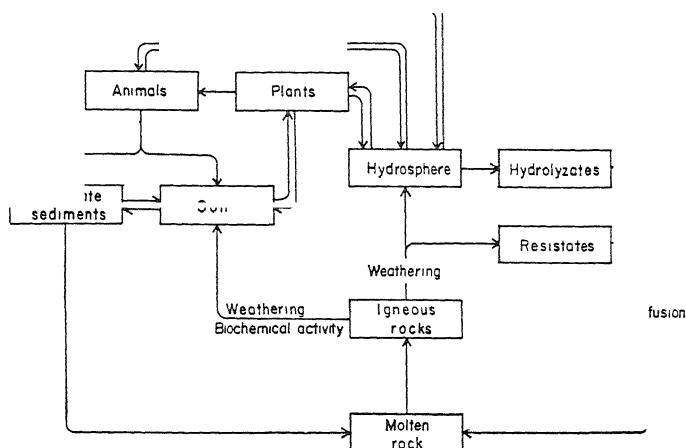


FIG. 24.1.—The cycle of phosphorus

CYCLE OF PHOSPHORUS

The cycle of phosphorus is presented in Figure 24.1. During weathering, phosphorus is largely liberated from minerals. The weathering solutions contain alkali phosphates and dissolved or colloidal calcium phosphate. A part of the phosphorus is soon reprecipitated as calcium phosphate, but the bulk is carried to the sea. Calcium phosphate is soluble in carbon dioxide-bearing water and probably also in waters rich in organic material. Some phosphorus seems to be released in juvenile waters. Tagueva (1942) found phosphorus (and arsenic) concentrated in waters connected with volcanic activity, whereas surface waters, with the exception of soda lakes, were deficient in this element.

A number of secondary phosphate minerals are formed by phosphate-bearing solutions. This group includes, among others, pyromorphite, $Pb_5[Cl|(PO_4)_3]$; the rare-earth phosphate weinschenkite,

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(Y,Er)[PO₄]·2H₂O; vivianite, Fe₃²⁺[PO₄]₂·8H₂O, which is often found in bog iron ores, cavities of fossils, etc., but also as a constituent of copper and tin veins; and turquoise, CuAl₆[(OH)₂|PO₄]₄·4H₂O. In addition, the group of uranites (uranmicas) includes a number of phosphate minerals, viz., torbernite, Cu[UO₂|PO₄]₂·8H₂O, and the calcium (autunite), magnesium (saléeite), and barium (uranocircite) compounds of corresponding composition (see also chap. 30).

Notable amounts of phosphorus are also transported into the sea in sewage, and finely divided rock powder containing phosphate minerals is believed to be an important source of phosphorus in the Arctic and Antarctic seas.

The content of phosphorus in sediments and their derivatives is illustrated in the accompanying tabulation by the analyses of composite samples, made by H. N. Stokes and G. Steiger and quoted from Clarke (1924; see also Table 5.52).

Rock	P ₂ O ₅ (Per Cent)
Sandstones	0.08
Red clay	0.30
Shales	0.17
Limestones	0.04

A considerable part of phosphorus remains in the resistates as undissolved apatite, monazite, and xenotime, and probably also in the structures of silicate minerals, such as garnet, which is stable against weathering. However, the bulk of phosphorus is deposited in the hydrolyzates as reprecipitated calcium phosphate. Phosphorus is enriched in the red clay which contains two and a half times as much P as do the igneous rocks. The phosphorus content of the carbonate sediments is rather small.

The analyses of river and lake waters collected and published by Clarke (1924) show that the content of phosphorus is usually low. As a matter of fact, the content of phosphorus in fresh water commonly does not exceed 5–10 mg/m³ (as phosphate), and consequently its determination is often neglected. Therefore, no phosphorus value is included in the average analyses of lake and river waters presented in Table 6.7.

In spite of the constant addition of phosphates to the sea, the content of phosphorus in ocean water remains low (see Table 6.17). Phosphorus is being continually removed from sea water. A part of the depletion is evidently caused by the action of organisms discussed above. The distribution of phosphorus in the sea is therefore notably

controlled by organic agencies. However, inorganic processes are also operative in the removal of phosphorus from sea water. The content of phosphorus in the upper layers of the sea is considerably lower than in the deep waters. The reason is the removal of phosphate by marine organisms. In addition, according to Dietz, Emery, and Shepard (1942), it is probable that sea water deeper than a few hundred meters is essentially saturated with $\text{Ca}_3(\text{PO}_4)_2$. If the ocean is saturated with tricalcium phosphate, an amount of phosphorus equal to that carried annually to the seas by rivers must be precipitated. Because the phosphate saturation point depends on the pH, changes in biological or physicochemical conditions may affect the concentration of the phosphate ion and consequently cause solution or precipitation of phosphate. As pointed out by Dietz, Emery, and Shepard, the calcium phosphate balance in the sea is similar in this respect to that of calcium carbonate (see chap. 15).

It seems to be probable that phosphate deposits are relatively common on the ocean floor. Both inorganic precipitation of calcium phosphate and biochemical processes may take place in their formation. According to Dietz, Emery, and Shepard (1942), the phosphate nodules which are often found abundantly in some shallow areas have been largely deposited inorganically from a colloidal suspension. The stagnant waters deficient in oxygen may allow the concentration of phosphorus in the absence of organisms which consume this element, and thus it will be precipitated as phosphate nodules or continuous beds. In addition, fluorine may be operative in the precipitation of phosphorus by making the calcium phosphate more or less insoluble. It is known that tricalcium phosphate absorbs fluorine from ground water.

The phosphate concretions are rather high in phosphorus; the authors cited above report an average content of 67 per cent $\text{Ca}_3(\text{PO}_4)_2$ in phosphate nodules off the coast of southern California. The fluorine content of these nodules was found to be 2.47–3.36 per cent. Collophane, the microcrystalline carbonate-fluorapatite, is the main constituent of the nodules. Francolite, another member of the apatite group, probably accompanies collophane in the nodules. It should be noted that many elements, e.g., zinc, cadmium, indium, and bismuth, become enriched in marine phosphates.

Phosphorus is also removed from the sea in the skeletal structures of marine organisms, many of which may be very high in phosphorus. The analysis of the phosphatic brachiopod quoted in Table 8.3 shows

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a content of 75.17 per cent tricalcium phosphate in the skeletal material. In the calcareous skeletons the phosphate content, however, is very much lower. According to Clarke and Wheeler (1922), vertebrate skeletons may form a more important source of phosphorus in sediments than invertebrate remains.

Secondary enrichment of phosphorus may take place in phosphatic sediments. Thus phosphates may become concentrated when carbonates are leached away from phosphate-bearing calcareous sediments and phosphatic limestones. On the other hand, ammonia derived from decaying marine organisms may dissolve phosphates, which may replace carbonates in limestone.

Still another part of phosphorus is, at least temporarily, removed from the cycle during the accumulation of guano. Guano consists of excrements and remains of animals, chiefly sea birds. It accumulates in dry areas, the largest deposits being found in Pacific islands and elsewhere in the belt of the trade winds. Fresh guano consists of a mixture of various phosphorus- and nitrogen-bearing organic substances and animal remains. Its composition changes constantly, and a number of nitrate, phosphate, oxalate, and urate minerals are produced, many of which are removed shortly after their formation through leaching and bacterial action, and only the sparingly soluble constituents remain in the guano beds. Calcium phosphates often become enriched in guano by these processes. The minerals found in guano include, among others, the phosphates monetite, $\text{CaH}[\text{PO}_4]$, and other acid calcium phosphates; struvite, $(\text{NH}_4)\text{Mg}[\text{PO}_4] \cdot 6\text{H}_2\text{O}$; stercorite, $(\text{NH}_4)\text{NaH}[\text{PO}_4] \cdot 8\text{H}_2\text{O}$; and the oxalate oxammite, $(\text{NH}_4)_2[\text{C}_2\text{O}_4] \cdot 2\text{H}_2\text{O}$. No older than Recent guano deposits are found in the geological column. Sometimes limestones and even igneous rocks are phosphatized by percolations from guano deposits.

The quantitative cycle of phosphorus was discussed by Goldschmidt (1922), who pointed out that all phosphorus liberated during weathering should be contained in sea water and in sediments. When the Earth as a whole is considered, it appears that the proportion of phosphorus present in the phosphate sediments must be rather small. The phosphorus found in the biosphere does not suffice to fill the deficit, and therefore Goldschmidt suggested that the deep ocean waters are enriched in phosphorus and consequently represent a blind alley in the cycle of this element, being unable to sustain life and displaying a lack of circulation.

ORES OF PHOSPHORUS

The phosphate concretions mentioned in the previous paragraph often are abundant constituents of sediments and sedimentary rocks ranging from Cambrian to Pleistocene. They grade frequently into continuous phosphorite beds, which are used as ores of phosphorus. The beds are never pure; their phosphate content may be 35 per cent or more. The best-known phosphorite deposits occur in England, Russia, Tunis and Algiers in Africa, and Idaho, Tennessee, and Florida in the United States. Guano deposits also have importance as sources of phosphate. Along with the sedimentogenic phosphorites, apatite forms an important source of phosphorus. Apatite is obtained from magmatic iron ores (e.g., Kiirunavaara in northern Sweden), gabbro pegmatites (southern Norway), nepheline syenite pegmatites (Chibina Tundra in Kola Peninsula, Russia), and contact metamorphic limestones (Canada).

VANADIUM

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

VANADIUM is one of the more abundant trace elements. Its abundance values in iron meteorites, silicate meteorites, and igneous rocks are presented in Table 25.1.

Table 4.1 shows that vanadium is rather strongly concentrated in pig iron in ore-smelting furnaces. In the separated sulfides its concentration is low, but in the silicate slag noteworthy quantities of vanadium are present. The same rule is valid for the meteorites. Table 4.2 shows that vanadium is strongly concentrated in the silicate phase. In the troilite phase of the iron meteorites, however,

TABLE 25.1
ABUNDANCE OF VANADIUM

Material	V (g/ton)
Iron meteorites (Noddack and Noddack, 1930).....	6
Silicate meteorites (Goldschmidt and Bauer; in Goldschmidt, 1937 <i>b</i>).....	50
Igneous rocks (Goldschmidt, 1937 <i>b</i>).....	150
Igneous rocks, average, Dutch East Indies (van Tongeren, 1938)	168
Igneous rocks, average (Lundegårdh, 1946).....	315

vanadium is concentrated in relation to the iron phase. The relative concentration of vanadium in terrestrial igneous rocks is still higher. These facts show that the general geochemical character of vanadium is pronouncedly lithophile, although not without a relatively distinct siderophile tendency, as pointed out by Leutwein (1941). Nothing suggests the chalcophile tendency of terrestrial vanadium, but it has distinct biophile trends. Vanadium is a notable constituent of the solar atmosphere.

Vanadium is a member of the iron family (Goldschmidt, 1929) or the ferrides (Landergrén, 1943).

VANADIUM IN IGNEOUS ROCKS

In the upper lithosphere, vanadium is oxyphile. The behavior of vanadium in igneous rocks is largely governed by the fact that it oc-

curs in three stable oxidation states in igneous surroundings, viz., as tri-, quadri-, and quinquevalent vanadium. All these, particularly V^{5+} , show a tendency to form complexes with oxygen and partly also with sulfur. These facts account for the relatively large number of vanadium minerals in general and for the extensive possibilities of diadochic substitution of various elements by vanadium in mineral structures.

Owing to its position in the Periodic System, vanadium resembles its neighbors, phosphorus and titanium, in its manner of occurrence, but notable differences also exist between the three elements in this respect. Vanadium is characteristic neither of the early magmatic pyrrhotite-pentlandite assemblages nor of late magmatic sulfides. According to Noddack and Noddack (1931a), the vanadium content of primary magmatic sulfides is 40 g/ton. The vanadium sulfide patronite, $VS_4(?)$, with up to 24 per cent V, and the complex copper sulfovanadate sulvanite, Cu_3VS_4 , are found in Nature, but they are rare and probably of secondary origin. On the other hand, vanadium is often strongly enriched in titaniferous iron ores, which represent the early-separated oxides. Vanadium, as a matter of fact, was discovered, in 1830, by N. G. Sefström, the Swedish chemist, in iron made of titaniferous iron ore. Like titanium and phosphorus, vanadium also tends to become concentrated in basic rocks, particularly in the basic segregations of gabbroic magmas, but no definite relationships exist between vanadium and phosphorus. Landergren (1948) reports 1,400 g/ton V in titaniferous and apatite-bearing iron ores of Sweden, whereas the content found by him in other iron ores of metamorphic rocks is only from 13 to 85 g/ton V.

The highest vanadium content in igneous rocks is found in those formed during the initial steps of the main stage of crystallization. The content of vanadium in igneous rocks is presented in Table 25.2.

In igneous rocks vanadium usually does not form independent minerals but is concealed in the structures of other minerals. The only exception is ardennite $Mn_4(MnAl_5)[(OH)_2](V,As)O_4 \cdot (SiO_4)_5 \cdot 2H_2O$, a rare member of the epidote-zoisite group. Tri-, quadri-, and quinquepositive vanadium ions occur in minerals of igneous rocks; their radii are 0.65, 0.61, and approximately 0.4 kX, respectively. Bivalent vanadium is a strong oxidizing agent; the radius of V^{2+} is unknown. According to Leutwein (1941), the radius of V^{5+} should be around 0.5 kX. The size of the V^{3+} ion is close to that of the Fe^{3+} ion (radius 0.67 kX), but the diadochic replacement in this case, accord-

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ing to Leutwein, is not very probable. The reason is that the trivalent vanadium is a comparatively strong reducing agent, which, if present, would reduce ferric iron to the ferrous state. This is also shown by the redox potentials of the ions in question (Ščerbina, 1939). The quadrivalent vanadium, on the other hand, is more plentiful in igneous rocks and readily replaces Ti^{4+} (radius 0.64 kX), Fe^{3+} , and probably also Al^{3+} (radius 0.57 kX). Quinquevalent vanadium is present in sediments and sedimentary rocks, in which the redox potential is higher than in igneous rocks. It replaces aluminum, preferably in clay minerals.

According to Ramdohr (1940), vanadium is largely found in magnetite when present in igneous rocks. On the other hand, Lebedev

TABLE 25.2
CONTENT OF VANADIUM IN IGNEOUS ROCKS

Rock	V (g/ton)
Basement Complex of southern Lapland (Sahama, 1945b):	
Ultrabasics	17
Gabbros and dolerites	56
Granites	17
Syenites	34
Granites and granodiorites (Leutwein, 1941)	1-20
Basic igneous rocks, central Roslagen, Sweden (Lundegårdh, 1946)	320
Acidic igneous rocks, central Roslagen, Sweden (Lundegårdh, 1946)	30

and Lebedev (1934) concluded that it is primarily concealed in ilmenite rather than in silicate minerals, but, according to Leutwein (1941), such is not the case; the titanian magnetites, on the other hand, are rich in vanadium and reportedly contain up to 0.41 per cent V. According to Landergren (1948), common magnetite may contain as much as 0.23 per cent V. Along with titanian magnetite, other titanium minerals of igneous rocks also contain vanadium in their structures, evidently as V^{4+} ions, replacing Ti^{4+} . Vanadium occurs in sphene and rutile; Leutwein (1941) reports about 0.5 per cent V in rutile. It should be noticed that VO_2 crystallizes in the rutile type.

In apatite, V^{5+} may replace P^{5+} (radius 0.35 kX). This explains the concentration of vanadium in the apatite-rich iron ores observed by Landergren (1948). Only in these ores and in the titaniferous iron ores does the content of vanadium correspond to that found in marine iron-bearing sediments.

The feldspars, which are the most important rock-making silicate minerals of igneous rocks, are nearly entirely devoid of vanadium. The dark constituents—pyroxenes, amphiboles, micas, etc.—on the other hand, almost always carry some vanadium as V^{4+} and V^{5+} ions, which replace Fe^{3+} and Al^{3+} . Augite and hornblende contain up to 680 g/ton V. Oftedal (1939*b*) found 3,080 g/ton V in phlogopite, and Bray (1942*b*) reported up to 1,000 and 640 g/ton V in granite biotites and muscovites, respectively. The distribution of vanadium among the femic and salic minerals of igneous rocks is illustrated by Bray's (1942*a*) analyses of minerals of a biotite monzonite: 670 g ton V in biotite and 7 g/ton in plagioclase.

Like phosphorus and arsenic, the quinquivalent vanadium has a pronounced tendency to form $[VO_4]$ tetrahedra in mineral structures. These complex anions are analogous to the complex $[PO_4]$ and $[AsO_4]$ anion tetrahedra.

So far, nothing is known about the possibilities of migration and concentration of vanadium as volatile compounds and in hydrothermal solutions. In hydrothermal assemblages, vanadium is known only as an accessory constituent of uraninites in the Ni-Co-U veins, the maximum content being 500 g/ton V (Leutwein, 1941).

VANADIUM MINERALS OF SECONDARY ORIGIN

Although no independent vanadium minerals are found in igneous rocks, vanadium may become strongly enough concentrated in sediments and sedimentary rocks to cause the occurrence of a number of independent minerals. In these surroundings the redox potential is higher than in igneous rocks, and therefore the minerals in question are vanadates. Geochemically, they are comparatively rare, and most of them are nothing but mineralogical curiosities because the conditions ruling their formation are met only seldom in Nature. Vanadium found in these minerals comes from vanadium-rich ground waters or from thermal waters. The chief metals found in these vanadates are calcium, manganese, (ferric) iron, uranium, lead, copper, and zinc. Bismuth also occurs as their constituent. These minerals are often accompanied by compounds of phosphorus, arsenic, and uranium. They are either simple vanadates, e.g., pucherite, $Bi[VO_4]$, and steigerite, $Al[VO_4] \cdot 3H_2O$, or complex vanadates, such as descloizite, $Pb(Zn,Cu)[OH|VO_4]$ (with 20–22 per cent V_2O_5); hewettite and meta-hewettite, $CaH_2[V_6O_{17}] \cdot 8H_2O$; vanadinite, $Pb_5[Cl|(VO_4)_3]$ (with 8–21 per cent V_2O_5 , isomorphic with apatite

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and a member of the apatite group); carnotite, approximately $K[VO_2|VO_4] \cdot 1\frac{1}{2}H_2O$ (contains about 21 per cent V_2O_5); tyuyamunite, $Ca[VO_2|VO_4]_2 \cdot 4H_2O$; and roscoelite, the vanadoan muscovite, in which Al^{3+} is diadochically replaced by V^{5+} in octahedral co-ordination (Wells and Brannock, 1946). Roscoelite is the high-vanadium end-member in the series in which muscovite is the aluminian end-member.

Carnotite and tyuyamunite are members of the uranite group (see chap. 30).

VANADIUM IN THE BIOSPHERE

Vanadium is found in numerous plants, which take it up from soil, where its content is 20–1,000 g/ton V (Mitchell, 1944). Bøggvad and Nielsen (1945) report contents varying from 2.7 to 7 g/ton V in Danish brown coals. Vanadium is also enriched in coal ashes: some coals from Argentina contain up to 21.4 per cent V in their ashes. Like molybdenum and tungsten, vanadium promotes the assimilation of nitrogen by soil micro-organisms. However, so far it cannot be stated whether or not vanadium is essential to organisms.

Vanadium is a frequent microconstituent of terrestrial animals, and it may promote the oxidation of lipides in them. Certain marine organisms are known which are able to collect exceptionally high amounts of vanadium from sea water. Some holothurians (e.g., *Stichopus Moebii*) and ascidians contain vanadium in their blood. The blood of the ascidians contains 10 per cent V in a 3 per cent solution of sulfuric acid, and the content in the blood of the holothurians is 10.4 per cent V. Vanadium is a characteristic constituent of the blood of both these classes of animals. However, contrary to previous belief, it has no role as a respiratory pigment. When the vanadium-bearing organisms perish, vanadium may accumulate in the bottom mud, but the role of animals in concentrating vanadium in sediments must be negligible because their vanadium content is very low.

Vanadium is also present in petroleum. A Persian crude oil is reported to contain as much as 2.82 per cent V. The vanadium content increases during the oxidation of the unsaturated petroleum hydrocarbons and their contemporaneous condensation and polymerization, whereby asphalt is finally produced. The maximum content in asphalt ashes is 43.4 per cent V. Shungite, the pre-Cambrian "carbonized" hydrocarbon from eastern Fennoscandia, contains up to 670 g/ton V in its ashes (Rankama, 1948a). As emphasized by Gold-

schmidt (1937a), vanadium is an effective catalyst in the industrial synthesis of hydrocarbons, and it may also be active in Nature in facilitating the reactions between hydrogen sulfide and organic substances. As in the case of nickel and molybdenum, so in the case of vanadium, valence forces and other special atomic properties control the association of the metals and the hydrocarbons. In the hydrocarbons these metals are present as organometallic compounds which are able to migrate with the hydrocarbons. A number of porphyrin complexes of vanadium have been found in petroleum, asphalt, and bituminous rocks. They are stable against chemical and physical agents and consequently prevent the removal of vanadium from these rocks.

Bader's (1937) averages of vanadium contents of bioliths are reproduced in Table 25.3. These values show that vanadium becomes partially mobilized during metamorphism.

TABLE 25.3
CONTENT OF VANADIUM IN BIOLITHS

Material	V (g. ton)
Asphalt, average.	5,400
Bituminous phosphates, average	1,600
Coal, average	900
Graphite, average.	200

CYCLE OF VANADIUM

The cycle of vanadium is characterized by the fact that its solution and migration take place only at a relatively high redox potential. The V^{3+} ion is a cation of the hydrolyzates in Goldschmidt's classification (see chap. 5), but it is readily oxidized to V^{5+} , which shows a tendency to form anion complexes. The biophile properties of vanadium also affect its cycle.

During the weathering of igneous rocks much vanadium is incorporated in the clay minerals formed. It remains therein as long as its host minerals are unchanged, still under the first stages of diagenetic and metamorphic processes. Therefore, the weathering solutions in a humid climate are poor in vanadium. A little vanadium seems to be extracted from the clay minerals by humic solutions. Vanadium is present in mineral waters, but it might be largely of juvenile origin in them. In arid regions, however, vanadium is concentrated in the aluminum hydroxide, being thus released during the decomposition of clay minerals. Quinquevalent vanadium is easily mobilized, and if heavy metals are present in ground waters and weathering solutions,

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rich local concentrations of lead, copper, zinc, and uranium vanadates may be formed, particularly in the zone of oxidation and in the presence of calcitic and dolomitic limestones, which make the pH suitable for the precipitation of the vanadates. Vanadium may also become adsorbed from relatively concentrated weathering solutions into sediments of arid regions.

Another possibility of the concentration of vanadium in sediments is its transportation, mostly in low concentrations, as vanadate in weathering solutions, which, under reducing conditions, usually in the presence of hydrogen sulfide, precipitate their vanadium as V_2S_5 in bituminous shales, asphalts, and similar rocks.

The content of vanadium in sediments and sedimentary rocks is illustrated by the analyses presented in Table 25.4.

In sea water, at least in the oxygen-rich upper layers, vanadium is present in the quinquevalent state. This vanadium is incorporated and partly concentrated in hydrolyzates and oxidates, whereas the precipitates and evaporates are notably devoid of vanadium. Phosphate sediments are also low in vanadium, and no quantitative relationship exists between the phosphorus and the vanadium content of sediments, contrary to previous belief (Jost, 1932). In sandstones the vanadium content is higher, the more argillaceous material is incorporated. If feldspar is present (proving the lack of chemical weathering), the vanadium content of sandstones, according to Jost, is very low.

Jost (1932) established the presence of regional differences in the vanadium content of limestones. Bituminous limestones are higher in vanadium than are other types. As a rule, the calcitic and dolomitic limestones are decidedly poorer in vanadium than are the hydrolyzate sediments. In glauconite-bearing sediments and in oxidates the vanadium content is higher than the average in the hydrolyzates. According to Palmqvist (1935), the content of vanadium in pure siderite is considerably lower than in siderite sediments containing iron silicates. In like manner in calcium carbonate- and iron carbonate-bearing marine iron ores the vanadium content decreases as the content of carbonate minerals increases.

The vanadium content of sedimentary iron ores often exceeds the vanadium average of hydrolyzates. According to Landergren (1948), oolite and laterite ores contain more vanadium than the upper lithosphere does, on an average. However, bauxites derived from acidic igneous rocks show a deficiency in vanadium, whereas those derived

from basic igneous rocks, on an average, are a little higher in vanadium than are their parent-rocks. Laterites and bauxites adsorb anions, whereas cations are principally taken up by clays, in which the presence of silica causes an excess of negative charge. It is probable that vanadium is adsorbed by laterites and bauxites in the form of the vanadate ion, whereas in clays it occurs as a cation in the clay minerals, as in roscoelite. Vanadium may partly become introduced into laterites and bauxites along with iron in weathering solutions.

Clays and shales containing organic matter are regularly higher in vanadium than are those devoid of such matter. The origin of the organic material, whether humic, coaly, or bituminous, does not

TABLE 25.4

CONTENT OF VANADIUM IN SEDIMENTS AND SEDIMENTARY ROCKS

Rock	V (g./ton)
Sandstones, average (Jost, 1932).....	20
Clays and shales, average (Jost, 1932).....	120
Calclitic and dolomitic limestones, average (Jost, 1932)	<10
Bauxite, average (Jost, 1932).....	600
Phosphorite and guano (Jost, 1932).....	<10
Sandstones, rich in iron oxide (Jost, 1932).....	up to 500
Greensand (Jost, 1932).....	220
Bituminous schist (Lundegårdh, 1946).....	1,000
Glauconite (Palmqvist, 1935).....	68
Oolitic and siliceous iron ores, average (Landergren, 1948).....	500
Siderite ores, average (Landergren, 1948).....	70
Bog iron ores, average (Landergren, 1948).....	<10
Laterite and bauxite ores, average (Landergren, 1948)	400

make any difference in this respect. A high content of vanadium is also present in the more or less metamorphosed derivatives of these sediments. The original sediments, e.g., muds, are usually highly reducing, and therefore in them vanadium is reduced to a lower state of oxidation, being frequently precipitated as sulfide, V_2S_5 , which is sparingly soluble. Bacteria may often be helpful in this process, which results in the separation of vanadium from iron and the other ferrides. Vanadium salts may also be precipitated in the presence of limestone.

Although Jost (1932) found that the content of vanadium in bituminous sediments increases with the content of bitumen, this observation was not confirmed by Assarsson (1941), who stated that the content of vanadium (up to 2,600 g./ton) and of molybdenum and tungsten in Swedish alum shales is not proportional to the content of organic matter. He suggested that these metals are probably com-

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bined with sulfur. In like manner, Bøgvad and Nielsen (1945) found no proportionality between the vanadium content of alum shales and their content of organic matter. In addition, the sulfides found in these rocks were totally devoid of vanadium. According to these observations, it is evident that vanadium in bituminous shales occurs as porphyrin complexes. As emphasized by Bader (1937), the vanadium content of bioliths depends both on their porphyrin content and on the content of vanadium in weathering and other solutions; the weathering solutions are rich in vanadium, particularly under arid conditions. According to Bader, the formation of bioliths rich in vanadium starts with the precipitation of vanadium derived from weathering solutions as V_2S_5 and is followed by the formation of organic vanadium complexes, particularly porphyrin complexes.

TABLE 25.5
CONTENT OF VANADIUM IN METAMORPHIC ROCKS

Rock	V (g./ton)
Orthogneisses (Leutwein, 1939).....	5
Paragneisses (Leutwein, 1939).....	20-70
Quartzites, southern Lapland (Sahama, 1945b).....	5.6-34
Aluminum-rich schists, southern Lapland (Sahama, 1945b) ..	34-56
Carbonate rocks, southern Lapland (Sahama, 1945b) ..	1 7

VANADIUM IN METAMORPHIC ROCKS

According to Leutwein (1941), vanadium becomes partly mobilized in strong metamorphic processes (see also Table 25.3). However, the original character of the metamorphic rocks is still clearly shown by their vanadium content. Table 25.5 presents the vanadium content in a number of metamorphic rocks. According to Leutwein (1939), the difference in the vanadium content of ortho- and paragneisses may be used to establish the igneous or sedimentary origin of gneisses.

ORES OF VANADIUM

No independent vanadium-ore bodies are found in igneous rocks because vanadium is scarce and does not form independent minerals during the differentiation. However, iron oxide ores contain vanadium as an accessory constituent, the highest contents being present in magnetite and titanian magnetite (average content < 0.2 per cent V). Vanadium may occur in the vanadiferous magnetite-ilmenite deposits as vanadian magnetite (coulsonite) with as much as nearly 5 per cent V. Oxide ores of iron may therefore be used as industrial sources of vanadium. The metal is recovered as a by-product during the metallurgical treatment of the ores. The most important

vanadium ores are of sedimentary origin. A relatively high redox potential is essential for their formation. Sedimentary iron ores (oxides) form the most important vanadium deposits. The minette ores contain up to 0.1 per cent V, and some ores at Krivorog in Russia contain as much as 0.5 per cent V (Leutwein, 1941). Patronite occurs at Minas Ragra in Peru. Lead, copper, and zinc vanadates are found in the Otavi area in southwestern Africa and at Broken Hill in northern Rhodesia. Carnotite and roscoelite occur in sandstones in Colorado and Utah in the United States, and tyuyamunite is found in Russian Turkestan.

Patronite occurs only at Minas Ragra. The deposit may have been formed through a natural distillation of petroleum hydrocarbons or through concentration of vanadium from vanadium-rich surface waters. Along with patronite, there occur hewettite and other calcium vanadates and the sulfate minasragrite, $V_2^{4+}[(OH)_2(SO_4)_2] \cdot 15H_2O$, in the oxidation zone of the deposit. According to Jost (1932), a plausible explanation of the origin of these deposits and of the association of vanadium with petroleum and asphalt in general is that vanadium sulfide, V_2S_5 , is formed when vanadate-bearing ground waters are brought into contact with hydrogen sulfide-bearing oils. The colloidal vanadium sulfide migrates with the oil and is finally precipitated by the action of carbon dioxide. The oil is oxidized into asphalt by atmospheric oxygen, and the vanadium sulfide acts as a catalyst in this process.

Vanadate minerals, such as carnotite, are disseminated in sandstones in southwestern United States, particularly in Colorado and Utah. The mineralization is most intense near shaly seams and clay galls in the sandstones. The actual cause of the concentration of vanadium in these deposits is still unknown. It has been suggested that some lower organisms might have been instrumental in concentrating vanadium, copper, uranium, silver, and selenium in these deposits. Another explanation is that soluble sulfates of these metals were present in ground and surface waters which were brought into contact with organic material. Sulfides of the metals were subsequently precipitated, and they were later oxidized under the formation of vanadates. Carnotite seems to be invariably associated with plant remains in these deposits. Along with carnotite, the deposits contain roscoelite, metaheewettite, and other vanadates of calcium, copper, and uranium. Chromium, barium, molybdenum, and arsenic are also present in the deposits. The carnotite-roscoelite ores contain 2-3.5 per cent V.

COLUMBIUM, TANTALUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

COLUMBIUM and tantalum form geochemically a rather coherent pair of elements. This fact is made evident by the difficulty of the separation of the two metals from each other during the course of chemical analysis. Owing to the lanthanide contraction, their ionic sizes are practically identical ($r_{\text{Cb}^{3+}} = 0.69 \text{ kX}$; $r_{\text{Ta}^{3+}} = 0.68 \text{ kX}$). Along with their chemical similarity and the similarity of their ionic charges and ionic types, this property causes them to occur commonly together in Nature, in analogy to the pair zirconium-hafnium and to the rare-earth metals. Rocks and minerals comparatively high in one are usually high in the other as well. However, in spite of the high degree of their chemical and geochemical similarity, columbium and tantalum are comparatively readily separated from each other in Nature and consequently are less coherent than the elements mentioned.

The average content of columbium and tantalum in igneous rocks is, according to Rankama (1944, 1948c), 24 g/ton Cb and 2.1 g/ton Ta. The average abundance ratio Cb:Ta is thus 11.4, but in some instances the normally less abundant metal of the pair may predominate in rocks and minerals.

Notwithstanding the chemical similarity between these metals and vanadium, which is due to their positions in the Periodic System, their manner of occurrence differs rather pronouncedly from that of vanadium.

There are no columbium and tantalum determinations to show the content of these elements in the sulfide phase of the meteorites, but the low quantities present in the silicate and metal phases and in terrestrial sulfides suggest that the content must be negligible. The sulfide minerals either are totally devoid of columbium and tantalum or carry only traces of the two metals, a fact which illustrates their strongly oxyphile character in the upper lithosphere.

COLUMBIUM, TANTALUM

Rankama (1944, 1948c) found the contents in meteoritic matter given in the accompanying tabulation.

	Cb	Ta	Cb Ta
	g./ton		
Silicate meteorites.	0 50	0 38	1 3
Meteoritic irons	0 20	0 06	3 3

Both columbium and tantalum are purely and typically lithophile elements, as is evident from all available information regarding their geochemical character. In the Earth they are strongly enriched in the uppermost part of the lithosphere. Outside the Earth columbium has been detected in the Sun's atmosphere, and also tantalum is probably present therein.

COLUMBIUM AND TANTALUM IN IGNEOUS ROCKS

The average content of columbium and tantalum in the various groups of igneous rocks is presented in Table 26.1, which is based on values given by Rankama (1944, 1948c). The values in parentheses are the averages reported for columbium by Goldschmidt (1937a). The columbium and tantalum averages for diorites given by Rankama are evidently too low.

Table 26.1 affirms quantitatively the fact well known to mineralogists that columbium and tantalum are concentrated in late crystallates during the magmatic differentiation. This concentration is very pronounced in granites, and tantalum shows a maximum in these rocks. Columbium, although concentrated in granites, differs clearly from tantalum, and its highest contents are reached in syenites and nepheline syenites. The values presented in this table show distinctly that the columbium and tantalum content in basic and ultrabasic rocks is low as compared with the quantities met in granites. Consequently, the behavior of these metals during magmatic differentiation is not similar to that of vanadium. However, remarkably much columbium is present in ultrabasic rocks, evidently a consequence of their high titanium content and of the resulting replacement of CaTi by NaCb, whereby columbium is removed from the magma at a comparatively early stage (Niggli, 1932).

In normal igneous rocks of the calc-alkalic series the content of

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columbium and tantalum is too low to cause the formation of their independent minerals, and hence they, like vanadium, are concealed in the structures of other minerals. According to Goldschmidt (1937*b*), the content of columbium in many rocks is roughly proportional to the zirconium content, the Cb:Zr ratio being 1:10. Goldschmidt suggests that in silicate melts columbium forms complex ions containing oxygen or hydroxyl groups. Such ions, similar to those formed by zirconium, should be able to remain for a comparatively long time in the residual melt.

In structures of rock-making minerals, vanadium replaces mainly Fe^{3+} , but also Fe^{2+} and Mg^{2+} and other cations. In spite of the simi-

TABLE 26.1
AVERAGE Cb AND Ta CONTENT AND Cb:Ta RATIO
IN IGNEOUS ROCKS

Rock	Cb	Ta	Cb:Ta
	g/ton		
Monomineralic rocks	0.3	0.7	0.4
Ultrabasic rocks	16	1.0	16.0
Eclogites	3	0.7	4.3
Gabbros	19 (7)	1.1	17.3
Diorites	3.6 (20)	0.7	5.1
Granites	20 (30)	4.2	4.8
Syenites	30	2.0	15.0
Nepheline syenites	310 (100)	0.8	387.5
Basic alkalic rocks	10	1.2	8.3

larity of the ionic sizes, columbium and tantalum do not replace ferric iron in minerals to any considerable degree but preferably substitute for titanium, which closely corresponds to them in its ionic size ($r_{\text{Ti}^{3+}} = 0.69 \text{ kX}$; $r_{\text{Ti}^{4+}} = 0.64 \text{ kX}$). Both columbium and tantalum are enriched in independent titanium minerals. Sphene and perovskite may contain up to several per cent Cb_2O_5 , and a maximum of 0.1 per cent Ta_2O_5 is reported in sphene. The earth-acid elements are also concentrated in rutile and in biotite and other titanium-bearing silicate minerals. However, the early magmatic titaniferous iron ores show a decided impoverishment of columbium and tantalum in relation to titanium. In like manner the columbium and tantalum content in other high-temperature titanium minerals is rather low. Along with the diadochic substitution of titanium by columbium and tantalum the diadochy Zr-Cb and Zr-Ta is of geochemical importance.

Columbium and tantalum are commonly found in zircon in concentrations up to 2 per cent Cb_2O_5 and 0.4 per cent Ta_2O_5 . Other zirconiferous minerals, like wöhlerite, astrophyllite, eudialite, eucolite, and catapleite, may contain noteworthy amounts of the two elements. A maximum of more than 5 per cent Cb_2O_5 has been met in wöhlerite. Because of its wide distribution as an accessory constituent of igneous rocks, zircon is evidently one of the important carriers of columbium and tantalum. Hence it follows that columbium and tantalum are true satellites of both titanium and zirconium. Small amounts of the earth-acid elements may replace chromium and manganese in their independent minerals.

The most dominant and typical feature of the geochemistry of columbium and tantalum is their pronounced concentration in pegmatites. In granite and nepheline syenite pegmatites these metals are often enriched enough to cause the formation of a number of independent minerals, characterizing the pegmatites in question. Both columbium and tantalum are elements characteristic of granite pegmatites, whereas columbium clearly predominates in nepheline syenite pegmatites. In spite of their close chemical and geochemical similarity, the earth-acid metals are frequently separated from each other in the pegmatites, although the reason often may be found in their original abundance relationships. Some pegmatites, e.g., in Nigeria, are known to carry nearly exclusively columbium and only small amounts of tantalum, whereas in other instances the case is just the reverse, and tantalum predominates, as in the western Australian tantalite pegmatites. In the pegmatites the two metals often occur closely connected with the rare-earth metals. Many of the most characteristic rare-earth minerals are columbates and tantalates, which usually also contain titanium and zirconium. When present in pegmatites, antimony and bismuth are sometimes connected with the earth-acid elements. The most important columbates and tantalates found in pegmatites include the minerals listed in Table 26.2.

Columbite and tantalite are the most widespread and abundant of these minerals. Pure columbite contains 82.7 per cent Cb_2O_5 , and tantalite contains 86.1 per cent Ta_2O_5 . All the species listed in Table 26.2 are chemically rather complicated, and their composition is variable. Often their crystal structures have disintegrated. Mossite and tapiolite are isomorphic with cassiterite, SnO_2 , and form a continuous series of mixtures with this mineral. Dysanalite is isomorphic

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with perovskite, CaTiO_3 , as is pyrochlore; but in the pyrochlore-perovskite series the miscibility is limited. The minerals listed in the first five groups of Table 26.2 are, in crystal chemical respects, grouped among the oxides. Fergusonite, on the other hand, is structurally related to scheelite. As a matter of fact, scheelite may contain traces of columbium; and both columbium and tantalum usually occur in wolframite and also in cassiterite. According to Goldschmidt

TABLE 26.2
COLUMBIUM AND TANTALUM MINERALS
FOUND IN PEGMATITES

	PEROVSKITE GROUP
Dysanalite,	$(\text{Ca,Ce,Na}, \dots)(\text{Ti,Fe,Cb})\text{O}_3$
	PYROCHLORE GROUP
Pyrochlore,	$(\text{Ca,Na})_2\text{Cb}_2\text{O}_6(\text{F,OH,O})$
Microlite,	$(\text{Ca,Na})_2\text{Ta}_2\text{O}_6(\text{O,OH,F})$
	RUTILE-MOSSITE GROUP
Mossite,	$(\text{Fe,Mn})(\text{Cb,Ta})_2\text{O}_6$
Tapiolite,	$(\text{Fe,Mn})(\text{Ta,Cb})_2\text{O}_6$
	BROOKITE-COLUMBITE GROUP
Columbite (niobite),	$(\text{Fe,Mn})(\text{Cb,Ta})_2\text{O}_6$
Tantalite,	$(\text{Fe,Mn})(\text{Ta,Cb})_2\text{O}_6$
	EUXENITE-BLOMSTRANDITE GROUP
Euxenite (polycrase),	$(\text{Y,Er,Ce,U,Pb,Ca})[(\text{Ti,Cb,Ta})_2(\text{O,OH})_6]$
Blomstrandite (priorite),	$(\text{Y,Ce,Ca,Na,Th,U})[(\text{Cb,Ta,Ti})_2\text{O}_6]$
	FERGUSONITE-STIBIOTANTALITE GROUP
Fergusonite,	$\text{Y}(\text{Cb,Ta})\text{O}_4$
Stibiotantalite,	SbTaO_4
Bismutotantalite,	BiTaO_4
	SAMARSKITE GROUP
Samaraskite (yttrocolumbite),	$(\text{Y,Er})_4[(\text{Cb,Ta})_2\text{O}_7]_3$
Yttrotantalite,	$\text{Y}_4[\text{Ta}_2\text{O}_7]_3$
Simpsonite,	$\text{Al}_2\text{Ta}_2\text{O}_5$

and Peters (1931*b*), the columbium and tantalum content of wolframite and cassiterite is due to the presence of scandium and iron columbates and tantalates, viz., ScCbO_4 , FeCb_2O_6 , and the corresponding tantalum compounds in these minerals. In spite of the differences in the chemical composition, samarskite and yttrotantalite might structurally resemble fergusonite. In some rare silicate minerals found in pegmatites, columbium and tantalum, in addition, occur as cations outside the silicon-oxygen framework. Epistolite, $(\text{Na,Ca})(\text{Cb,Ti,Mg,Fe,Mn})[\text{OH}|\text{SiO}_4]$, and steenstrupine, probably $(\text{Na,Ca})_3\text{CaCe}(\text{Cb,Ta})[(\text{OH,F})|(\text{Si,P})\text{O}_4]_3$, are examples of such minerals.

Actually, the independent columbium and tantalum minerals

(columbates and tantalates) found in pegmatites are double oxides. No silicates are known which contain the earth-acid elements as major constituents. The reluctance of these metals to enter silicates is probably due to the fact that the Cb^{5+} and Ta^{5+} ions, like other quinquivalent and many trivalent cations, cannot form electrically neutralized structures of sufficient stability.

A small part of columbium and tantalum which is not separated during the pegmatitic stage of crystallization is enriched in pneumatolytic formations, e.g., in greisen, and crystallizes as columbates and tantalates, preferably with tin and tungsten, but sometimes also with uranium.

CYCLE OF COLUMBIUM AND TANTALUM

During the exogenic differentiation a large proportion of columbium and tantalum is accumulated in the hydrolyzate sediments at a comparatively early stage. This is due to the fact that the salts of these elements, which may be liberated during the weathering and be transported in the weathering solutions, are readily hydrolyzed. Such solutions carry columbium and tantalum probably as soluble alkali columbates and tantalates, and they deposit the two metals in clays. The content of the earth-acid metals in hydrolyzate sediments may be considerable: the Baltic clays are reported by Rankama (1944, 1948c) to contain as much columbium and tantalum as do granitic rocks, on an average. The highest columbium and tantalum contents among hydrolyzates are found in bauxites, laterites and kaolin (up to 0.07 per cent Cb_2O_3 and 0.01 per cent Ta_2O_5 in kaolin). Some columbium and tantalum is always present in the resistates because many of their independent minerals and other minerals accommodating them, for example, zircon, are stable against both mechanical and chemical weathering. Owing to their high specific gravity, the columbium and tantalum minerals are often enriched in placers. Such concentrates and the columbate and tantalate minerals found in pegmatites are used as ores of columbium and tantalum.

Another part of columbium and tantalum is present in sea water, although their concentrations must be very low. The two elements are deposited in marine carbonate sediments and in some evaporates: anhydrite contains a trace of columbium. The columbium content of the deep-sea manganese nodules sometimes shows an enrichment of columbium several times over its average content in igneous rocks.

OXYGEN

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

OXYGEN is geochemically a decidedly lithophile element. No oxygen is present in the metal and sulfide phases of the meteorites. In the metal phase all the elements are present in the form of alloy systems. Such elements as phosphorus, carbon, and silicon, which are combined with oxygen when found in the lithosphere, occur in meteoritic iron as phosphides (schreibersite), carbides (cohenite), or form solid solutions with iron. It is probable that the Earth's nickel-iron core is totally devoid of oxygen, which is quantitatively found in the uppermost geochemical spheres.

TABLE 27.1

ABUNDANCE OF OXYGEN

Material	O (Per Cent)
All meteorites.	32 30
Silicate meteorites.	42
Igneous rocks.	46 42
Hydrosphere	86
Atmosphere.	23 15

Some abundance values of oxygen are presented in Table 27.1. Oxygen is the most abundant of all elements found in igneous rocks, in silicate meteorites, and in meteorites as a whole. In the Sun's atmosphere oxygen occupies the third place in abundance right after hydrogen and helium (see Tables 2.3 and 2.5).

With reference to its terrestrial occurrence, oxygen is also strongly atmophile and, as an essential constituent of living matter, a pronouncedly biophile element.

OXYGEN IN THE UPPER LITHOSPHERE

In the upper lithosphere oxygen is the prototype of all oxyphile elements. The oxygen content of the upper lithosphere varies according to the composition of the constituent rocks. The oxygen con-

tent of the various groups of igneous rocks shown in the accompanying tabulation are obtained on the basis of the average compositions

Rock	O Per Cent.
Dunite	45.40
Hornblendite	43.06
Gabbro	45.11
Diorite	46.46
Granodiorite	47.88
Granite	48.53

presented by Daly (1933). These values show that in normal calc-alkalic rocks the oxygen content is lower in the basic rocks than in the acidic ones. The low oxygen content of basic rocks is of considerable geochemical importance. Petrological evidence shows that orthosilicates often predominate over metasilicates in igneous rocks formed during the earlier stages of the crystallization of a magma. The separation of iron and magnesium from the magma begins with the crystallization of olivine, $(\text{Mg,Fe})_2[\text{SiO}_4]$, whereas the orthorhombic pyroxenes, $(\text{Mg,Fe})_2[\text{Si}_2\text{O}_6]$, and other minerals do not crystallize until a later stage is reached. The orthosilicates of iron and magnesium contain less oxygen than do the corresponding metasilicates, as the percentages in the accompanying tabulation show.

Compound	O (Per Cent)
Mg_2SiO_4	45.5
MgSiO_3	46.2
Fe_2SiO_4	31.4
FeSiO_3	36.4

The deeper parts of the lithosphere, which correspond in chemical composition to gabbroic rocks, are evidently lower in oxygen than are the superficial parts. The value given in Table 2.3 for the average oxygen content of igneous rocks is 46.42 per cent. However, this oxygen does definitely not suffice to oxidize the electropositive elements to their highest state of oxidation, if hydrogen, for which no value is given in Table 2.3, is also taken into account. The inevitable result is that iron, in particular, is not completely oxidized to ferric iron but is present in rocks largely as ferrous iron, which forms, especially in basic rocks, ferromagnesian minerals. In like manner manganese is present as bivalent manganous ions, which replace ferrous iron and magnesium diadochically. The oxygen deficiency in the Earth is still more conspicuous if the deeper-lying geochemical shells are considered together with the lithosphere. According to the abundance calculations carried out by Goldschmidt (1937b), the oxygen deficiency

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in meteorites is rather high, all their phases being considered. Such is also the case if only their silicate phase is taken into account. It is evident that the ferrous iron content of silicate meteorites is very high, whereas only small amounts of ferric iron are present in them.

If the average content of oxygen in igneous rocks, 46.42 per cent by weight, is calculated as per cent by volume, the result is as high as 91.83 (Table 2.2). In the silicate phase of meteorites the oxygen content is 90.81 per cent by volume. The bivalent negative oxygen ion has a radius of 1.32 kX, whereas the radii of silicon and most of the cations are considerably smaller. As pointed out by Sir Lawrence Bragg in 1927, the unit cells of silicate minerals may be considered to consist essentially of oxygen anions linked together by cations. Therefore, the lithosphere is nothing else than an oxysphere (Goldschmidt, 1928). Actually, more than nine-tenths of the space occupied by the atoms in the rocks of the upper lithosphere are filled with oxygen.

The foregoing discussion shows that oxygen actually is the only important anion in the upper lithosphere. As emphasized by Goldschmidt (1928), all other quantitatively important elements either occur as cations or form anion complexes with oxygen.

OXYGEN IN THE HYDROSPHERE AND THE ATMOSPHERE

The bulk of the terrestrial oxygen is, without doubt, present in the lithosphere. However, a proportion of oxygen, even though not large, is located outside the solid crust of the Earth. This proportion is of very high geochemical importance. Combined with hydrogen in water, a part of this oxygen forms the hydrosphere, and another part is found in the atmosphere as one of its main constituents. Ozone and other oxygen compounds also found in the atmosphere were discussed in chapter 7. The amount of oxygen in these compounds is, geochemically speaking, negligible and may be omitted from the following calculations.

The quantities of oxygen in the hydrosphere and the atmosphere, expressed as kilograms per square centimeter of the Earth's surface are given in the accompanying tabulation. The second value is calcu-

	kg·cm ⁻²
Free oxygen in the atmosphere.....	0.230
Combined oxygen in the hydrosphere.....	251.1
Dissolved oxygen in the hydrosphere.....	0.002

lated from the facts given in chapter 6; the other two are from Goldschmidt (1933a). These figures show that the amount of oxygen in

the atmosphere is only about a thousandth part of the quantity present in the hydrosphere. It must also be taken into account that oxygen is one of the most important constituents of the biosphere because it is needed for almost all processes of life. However, the amount of oxygen contained in the biosphere is not readily calculated, but it can in no case match the quantity of oxygen present in the atmosphere.

The atmospheric oxygen is the most active of all terrestrial oxygen. This element combines readily with almost all other elements to form oxides. Therefore, it appears rather strange that uncombined oxygen can be present at all in the atmosphere. One would prefer to presume that every trace of oxygen liberated in chemical processes would combine, sooner or later, with other elements, thereby reducing the content of oxygen in the atmosphere practically to zero. According to the opinion of Goldschmidt (1934, 1937*b*), the primordial atmosphere contained only very little oxygen or none at all. A proof of this assumption is the rarity of oxygen in volcanic gases, which often are entirely devoid of oxygen or contain it only in small quantities. Therefore, it is evident that oxygen is not an essential constituent of magmatic emanations. If present, it may be of a vadose origin, i.e., carried to the locus of volcanic activity by ground waters.

Tammann (1924*b*) suggested that no free oxygen was present in the original gaseous shell surrounding the cooling Earth. The oxygen found in the present-day atmosphere was formed by the thermal dissociation of water vapor to oxygen and hydrogen during the first stages of the geological evolution of the Earth. The hydrogen dissipated into interplanetary space because of its high velocity of escape. A part of the liberated oxygen was consumed in the oxidation of the liquid silicate melt until a solid crust was formed. Tammann believed that this process was responsible for the generation of all oxygen now found in the atmosphere. The opinion of the passive enrichment of oxygen in the atmosphere was shared by Kuhn and Rittmann (1941; Kuhn, 1942; Rittmann, 1947). Tammann (1924*b*) also showed that at high temperatures, around the melting point of basaltic magma, and with a high partial pressure of water vapor in the atmosphere—a pressure of approximately 300 atm is developed on the evaporation of all terrestrial water and ice—the dissociation of water vapor is high enough to provide for all the free oxygen now found in the atmosphere. Later, Poole (1941) offered the suggestion that the photochemical dissociation of water vapor in the strato-

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sphere during the geological history of the Earth has caused the slow accumulation of oxygen in the atmosphere, which originally contained oxygen only in the form of water vapor. However, Wildt (1942b) has shown that this process is impossible, and also, in Poole's opinion, it would have produced only enough oxygen to allow the start of plant life; the bulk of the atmospheric oxygen would be a result of photosynthesis. This is in accordance with the opinion expressed by Goldschmidt (1934, 1937b) that the atmospheric oxygen has been largely formed as a result of activities taking place in the biosphere. Therefore, it seems reasonable to assume that a suitable initial supply of oxygen has been formed in the atmosphere by inorganic processes and that most oxygen has been generated by a rather slow process, viz., the photosynthetic activity of chlorophyll-bearing plants (see chap. 8) which has taken place during the geological history of the Earth. All oxygen now found in the atmosphere is certainly an accumulated by-product of the assimilation processes in green plants.

The oxygen separated during the photosynthesis is expelled into air or water. The greatest part of the carbon assimilated by the plants reunites with oxygen after their death and forms carbon monoxide and dioxide, but another part is converted to peat and, in the course of geological time, to brown coal and coal. Therefore, there remains free a quantity of oxygen which corresponds to the amount of carbon stored in the aforementioned bioliths and thus removed from the cycle. Consequently, the amount of oxygen in the atmosphere must at any time correspond to the amount of carbon present in the biosphere plus that preserved in the bioliths, according to the C:O ratio expressed by the formula CO_2 . Thus the amount of oxygen has increased during the geological evolution of the Earth until the present quantity was reached. The increase in the oxygen content of the air has evidently been one of the factors affecting the evolution of plants and animals from lower to more complicated forms.

Eskola (1939a) emphasized the fact that during the orogenic periods in the Earth's history the volcanic activity and the production of juvenile carbon dioxide attained a maximum which may have corresponded to a materially increased supply of oxygen and the well-established increased rate of organic evolution.

The presence of large amounts of free oxygen in the atmosphere is practically restricted to the Earth, as far as our Solar System is considered.

The present rate of photosynthetic activity on the Earth is capable of producing all the atmospheric oxygen within a few thousand years, thereafter maintaining the present oxygen level in the air. Therefore, a complete turnover of all atmospheric oxygen through photosynthesis is estimated to occur every few thousand years (Kamen, 1946).

FOSSIL OXYGEN

The discussion presented above shows that the cycle of oxygen is closely connected with the geochemical activity of the biosphere. The cycle of oxygen is also closely related to that of carbon and has been discussed with that element in chapter 19. When the cycle of oxygen is considered, the amount of free oxygen in the atmosphere must also be taken into account and likewise the quantity consumed in the

TABLE 27.2
FeO AND Fe₂O₃ CONTENT OF IGNEOUS ROCKS AND IN
SOME OF THEIR WEATHERING PRODUCTS

Material	Fe ₂ O ₃ (Per Cent)	FeO (Per Cent)	2Fe ₂ O ₃ :FeO
Igneous rocks.	3 08	3 80	0 73
Shales.	4 03	2 46	1 47
Terrigenous muds	5 07	2 30	1 98
Sandstones.	1 08	0 30	3 24

weathering processes and thus taken from the atmosphere. As a matter of fact, oxidation is one of the most important processes in the exogenic cycle.

The principal consumer of oxygen during weathering is iron, a large part of which is converted from the ferrous to the ferric state. In like manner, bivalent manganese is oxidized to the quadrivalent state. Still another consumer of oxygen is sulfur. This element is present in igneous rocks chiefly as sulfides, which are oxidized to free sulfuric acid and sulfates. The oxygen required in all these oxidation phenomena is called fossil oxygen; its amount was calculated by Goldschmidt (1933a).

Goldschmidt based his calculations on the content of FeO and Fe₂O₃ in igneous rocks, shales, terrigenous muds, and sandstones. The contents are given in Table 27.2. This table shows that the atomic ratio of ferric iron to ferrous iron is considerably lower in igneous rocks than in the sediments considered. The ratio is highest in sandstones (about 3.2) and lowest in shales (about 1.5) among the sedi-

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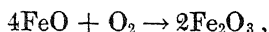
ments and their derivatives. On the basis of Table 27.2 the amount of ferrous iron may be calculated which must be oxidized to ferric iron in igneous rocks in order that the maximum and minimum ferric iron to ferrous iron ratios referred to above might be obtained. In order to reach the ratio 1.5, 1.18 per cent FeO in igneous rocks must be oxidized to Fe_2O_3 , whereas the content of 2.23 per cent FeO is required in order to reach the ratio 3.2. The quantities of oxygen needed in this oxidation process are then calculated, as well as the amounts of oxygen necessary to convert MnO to MnO_2 and S to SO_3 , the percentages being obtained in a calculation corresponding to that presented for iron. However, in the first case (ratio 1.5), only approximately one-third of manganese and sulfur will be considered to become oxidized, because sediments contain notable amounts of manganoous manganese and sulfur as sulfides. In the second case (ratio 3.2), the oxidation of sulfur and manganese is considered complete. The consumption of oxygen in all these cases is presented in Table 27.3.

The grand total of igneous rocks weathered during the geological history of the Earth amounts to $160 \text{ kg} \cdot \text{cm}^{-2}$. The following amount of oxygen is consumed during the weathering of this quantity of rocks; the value is calculated on the basis of those recorded in Table 27.3, as follows:

1. $0.253 \text{ kg} \cdot \text{cm}^{-2}$ oxygen is consumed, if the ratio of ferric iron to ferrous iron is assumed to be 1.5.
2. $0.562 \text{ kg} \cdot \text{cm}^{-2}$ oxygen is consumed, if the ratio is assumed to be 3.2.

The two values indicate the amount of fossil oxygen. Owing to the difficulties involved in the calculation of a reliable average chemical composition for sediments and their derivatives, these values represent only a maximum and a minimum. The value previously given for the amount of free oxygen in the atmosphere is $0.230 \text{ kg} \cdot \text{cm}^{-2}$ and for the quantity of oxygen dissolved in the sea, $0.002 \text{ kg} \cdot \text{cm}^{-2}$. It is therefore evident that the amount of fossil oxygen is considerably larger than the total amount of free oxygen in the uppermost geochemical spheres. From the foregoing values the grand total of free and fossil oxygen may be calculated to lie between 0.485 and $0.794 \text{ kg} \cdot \text{cm}^{-2}$.

Barth (1948) has calculated the quantity of oxygen consumed in the upper lithosphere in the reaction



provided that all ferrous iron in minerals is available for oxidation.

The mass of the atmosphere is approximately 52 Gg, and the amount of free oxygen (23.01 per cent by weight) found therein is thus about 12 Gg. The mass of the lithosphere down to a depth of 16 km (the "ten-mile crust")¹ is 190,000 Gg. The amount of FeO (3.80 per cent by weight) in the upper lithosphere is thus 7,220 Gg. The quantity of oxygen required to oxidize this amount of Fe₂O₃, calculated from the above-mentioned equation, is 804 Gg, and consequently the amount of free oxygen available in the atmosphere is only 1.43 per cent of the amount required. In other words, all atmospheric oxygen would suffice to oxidize iron only in 1.43 per cent of the uppermost crust, provided that the crust is homogeneous in composition. This percentage would correspond to a depth of less than 230 m, and, with reference to the oxidation of sulfur and manganese, the depth would

TABLE 27.3
CONSUMPTION OF OXYGEN IN SOME WEATHERING PROCESSES

CONSUMPTION OF OXYGEN (PER CENT)			
2Fe ₂ O ₃ FeO = 1.5		2Fe ₂ O ₃ FeO = 3.2	
1.18 per cent FeO, oxidized to Fe ₂ O ₃	0.131	2.23 per cent FeO, oxidized to Fe ₂ O ₃	0.249
0.03 per cent MnO, oxidized to MnO ₂	0.008	0.12 per cent MnO, oxidized to MnO ₂	0.027
0.013 per cent S, oxidized to SO ₃	0.019	0.05 per cent S, oxidized to SO ₃	0.075
Total consumption	0.158	Total consumption	0.351

be still shallower. Barth considers that under geologically stable conditions a lateritization all over the Earth would readily be possible, and thereby the atmosphere would be stripped of all its oxygen.

Along with its biochemical cycle, oxygen undergoes an inorganic cycle of equal importance (Barth, 1948). Highly oxidized sediments and surface rocks release their oxygen when brought to greater depths during orogenic movements. Oxygen returns to the Earth's surface in minerals, carbon dioxide, and water. Atomic oxygen may be formed by the dissociation of oxides at elevated temperatures and high pressures. A similar conclusion was reached by Landergren (1948), who emphasized the important role of oxygen in the endo-genic-exogenic migration of elements.

OXYGEN IN THE BIOSPHERE

Oxygen is an essential constituent of almost all living organisms. Its main importance lies in its role in respiration. In most cases, all

1. Goldschmidt (1937b) emphasizes the fact that the value of the ten-mile crust as a basis of quantitative calculations in geochemistry is questionable.

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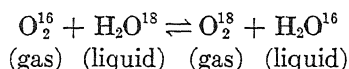
higher organisms require a continual supply of free oxygen. However, oxygen is a deadly poison to certain lower organisms, called obligatory anaerobes. Other lower organisms, chiefly bacteria, are unable to utilize free oxygen. Such anaerobic organisms use combined oxygen, obtained from complex organic molecules, as a source of energy in their biological activities.

Oxidation processes predominate in biochemical systems. The energy required by the organisms for their various activities is generated in the oxidation.

OXYGEN ISOTOPES

Three oxygen isotopes, viz., O^{16} , O^{17} , and O^{18} , are known to exist, O^{16} being the most abundant of them all. Owing to the very low abundance of O^{17} (see Table 2.7) the changes in the abundance of the heavy oxygen isotope are entirely attributed to O^{18} .

The heavy isotope, O^{18} , is somewhat concentrated in air as compared with its content in fresh water. The reaction



determines the final O^{18} content of atmospheric air. The cause of the O^{18} excess in air may be the photosynthetic liberation of oxygen, but there are also several other possible explanations. However, it is probable that all oxygen produced in photosynthesis comes from the dissociation of water and not from carbon dioxide (Kamen and Barker, 1945); and the heavy isotope O^{18} , reacting more slowly than the light one, O^{16} , may accumulate in the atmosphere.

Sea water also has a slightly higher O^{18} content than fresh water. This fact is caused by the isotope fractionation taking place during evaporation. Water from hydrated minerals (borates) is also higher in O^{18} than fresh water is.

According to Dole and Slobod (1940), there exists no significant difference between the isotopic composition of oxygen recovered from carbonate rocks of greatly differing geological age. Moreover, iron ores of sedimentary origin and sea water have materially the same O^{18}/O^{16} ratio. Fresh-water oxygen has the same O^{18} content as rocks and ores devoid of carbonates.

In carbonates the O^{18} content is a little higher than in fresh water. The O^{18}/O^{16} ratio in atmospheric oxygen is closer to the corresponding ratio found in carbonates than to that established for ocean water.

Oxygen in biological materials is often enriched in O^{18} .

CHROMIUM

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

NOTWITHSTANDING its even atomic number, chromium is a less abundant constituent of the solar atmosphere and of the upper lithosphere than is its odd-numbered neighbor in the Periodic System, manganese (see Table 2.3). In the meteorites the case is the reverse, and chromium is also more abundant than vanadium, in full agreement with the rule of Oddo and Harkins. Like the high abun-

TABLE 28.1
ABUNDANCE OF CHROMIUM IN METEORITES
AND IN IGNEOUS ROCKS

Material	Cr (g/ton)
Metal phase of meteorites (Goldschmidt and Peters, 1933 <i>b</i>).....	300
Troilite nodules of meteoritic irons (Goldschmidt and Peters, 1933 <i>b</i>).....	20,000
Troilite nodules of silicate meteorites (Goldschmidt, 1937 <i>b</i>).....	1,000
Silicate phase of meteorites (Merrill, 1916; recalculated by Goldschmidt, 1937 <i>b</i>).....	3,900
Igneous rocks (Hevesy, Merkel, and Wüstlin, 1934)	530
Igneous rocks (Goldschmidt, Bauer, and Hörmann in Goldschmidt, 1937 <i>b</i>).....	200
Igneous rocks, Dutch East Indies (van Tongeren, 1938).....	520
Igneous rocks, mainly from Sweden (Lundegårdh, 1946).....	35

dance of aluminum, the scarcity of chromium in the uppermost lithosphere also affords material proof of the origin of the lithosphere as a result of a pronounced differentiation process.

The general geochemical character of chromium is illustrated by the values of its abundance in the meteorite phases and in igneous rocks given in Table 28.1. The values recorded in this table establish the presence of a chromium maximum in the troilite nodules of iron meteorites. Chromium is usually contained therein as the sulfospinel daubréelite, FeCr_2S_4 . In the troilite nodules of silicate meteorites, on the other hand, chromium is less abundant. When distributed be-

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tween a metal phase and a sulfide phase, chromium is decidedly concentrated in the latter phase. In the metal phase chromium forms chromiferous spinels, notably chromite, FeCr_2O_4 , but its content is rather low. As soon as a silicate phase becomes available, the bulk of chromium will be incorporated therein. In silicate meteorites chromium occurs preferentially as chromian spinels, essentially chromite. It is therefore evident that the general geochemical character of chromium is not chalcophile, although the highest concentration of this metal is met in the sulfide phase of meteorites. The redox potential of the system in question is of high importance in the distribution of chromium, and its chalcophile character is pronounced only if oxygen is absent or when its amount does not suffice for the oxidation of all available chromium. In other cases chromium is lithophile.

A little chromium is present also in schreibersite. Goldschmidt and Peters (1933*b*) report a content of 100 g/ton therein.

The abundance of chromium in the upper lithosphere is still unsettled. According to Goldschmidt (1937*b*), the value given by Hevesy and co-workers is too high. On the other hand, it seems to be probable that the value obtained by Lundegårdh (1946) is decidedly too low.

Chromium is one of the ferrides (Landergren, 1943) and resembles iron geochemically in many respects.

CHROMIUM IN IGNEOUS ROCKS

The content of chromium in silicate meteorites is many times as high as that in igneous rocks, and therefore it follows that chromium is separated from the magma mainly during the earliest stages of differentiation. The changes in the chromium content in the various classes of igneous rocks are presented in Table 28.2. These values show that chromium, like titanium and phosphorus, is strongly enriched in the early crystallates. Its *E*-value must be high. Iron ores of igneous origin are often chromiferous, the cause being the presence of chromium in the magnetite structure. Landergren (1943, 1948) reports up to 5,500 g/ton Cr in titaniferous iron ores and 3,500 g/ton in magnetite ores found in gabbros. Chromium is also a normal and abundant constituent of the early-crystallized olivine rocks or dunites, as their average chromium content clearly shows. Chromite is, as a rule, the first mineral to separate during the normal crystallization of a calc-alkalic magma. In this respect its behavior departs from that of titanium and phosphorus. The dunites contain chromium

largely as chromite, but it may also be incorporated in the structures of other early-crystallizing minerals.

Sulfide minerals of chromium have, so far, never been observed in terrestrial rocks. In magmatic sulfides the average chromium content is 0.02 g/ton (Noddack and Noddack, 1931a). This value shows that chromium is strongly oxyphile in the upper lithosphere. In igneous rocks chromium occurs both in oxide and in silicate minerals. The only independent chromium minerals of these rocks are the chromian members of the spinel group, viz., magnesiochromite, MgCr_2O_4 , and chromite, FeCr_2O_4 , and their isomorphic mixtures. According to Stevens (1944), the major constituents of chromite also include Al^{3+} .

TABLE 28.2
CONTENT OF CHROMIUM IN IGNEOUS ROCKS

Rock	Cr (g/ton)
<i>Averages (Goldschmidt, 1937a):</i>	
Peridotite (dunite)	3,400
Gabbro	340
Diorite	68
Granite	2
Nepheline syenite	0.7
<i>Basement Complex of southern Lapland (Sahama, 1945b):</i>	
Ultrabasics	>2,000
Gabbros and dolerites	410
Granites	2-6.8
Syenites	200

In basic and ultrabasic rocks the chromian spinel occurs either as pure chromite or as picotite, $(\text{Mg,Fe})(\text{Al,Fe,Cr})_2\text{O}_4$, which consequently is a mixture of chromite and of the magnesium-aluminum spinel. If present in appreciable amounts, chromium, like titanium, enters the structures of many silicate minerals of petrological importance. In such silicates the Cr^{3+} ion replaces other metal ions diadochically. The following are important among such chrome minerals: chromian garnet or uvarovite, $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$; chromian diopside, with up to 2 per cent Cr; chromian epidote or tawmawite; chromian mica or fuchsite; and chromian chlorite or kämmererite. All these chromiferous silicates are relatively rare, and they are found as rock-making minerals only if the chromium supply available during their formation has been large. Therefore, their geochemical importance is not very great. More significant geochemically is the chromium present only in traces in the structures of silicate minerals. This chromium evidently represents the bulk of chromium in the upper lithosphere.

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Common augite and hornblende may contain nearly 1,400 g/ton Cr. Wager and Mitchell (1945) found 1,000 g/ton Cr in olivine from a gabbro picrite, and less than 2 g/ton in the same mineral from some later differentiates of a basic magma. In the clinopyroxene of an olivine gabbro they report 400 g/ton Cr, and less than 2 g/ton in the same mineral of later members of the differentiation series.

According to Lundegårdh (1946), much chromium may be incorporated in forsterite-rich olivine, whereas the fayalitic olivines are deficient in chromium. Probably Fe^{3+} at elevated temperatures is not readily replaced by Cr^{3+} . When magnesium-rich olivine and clinopyroxene occur together, chromium is preferentially concentrated in the latter. This is the case also if magnetite is substituted for olivine. At low temperatures the replacement of ferric iron by chromium seems to take place more readily. Bray (1942a) reports in granite biotites as much as nearly 1,100 g/ton Cr and in granite muscovites, up to 500 g/ton Cr.

Another common feature of chromium and titanium is their reluctance to form simple silicates. Chromium occupies two different structural positions in minerals. In chromates the sexpositive chromium forms a complex anion linking, like phosphorus and sulfur, four oxygen atoms to form a tetrahedral $[\text{CrO}_4]$ complex. Such complexes form independent groups in the structure. Crocoite, $\text{Pb}[\text{CrO}_4]$, is the most important representative of chromate minerals; the chromates are geochemically rather unimportant. On the other hand, chromium is present in minerals as the trivalent cation Cr^{3+} , with a radius of 0.64 kX. This radius is close to the radii of Al^{3+} (0.57 kX) and particularly Fe^{3+} (0.67 kX). In silicate minerals chromium is present as a cation outside the complex silicon-oxygen framework, and thereby readily replaces ferric iron and aluminum diadochically. This is the most important manner of occurrence of lithospheric chromium. However, the diadochic replacement of Al^{3+} by Cr^{3+} seems to be possible only if aluminum forms $[\text{AlO}_6]$ groups in the structure and does not replace silicon to form $[\text{AlO}_4]$ tetrahedra. The radius of the Cr^{3+} ion, like that of the Fe^{3+} ion, is too big to allow the substitution of Si^{4+} by Cr^{3+} in $[\text{SiO}_4]$ tetrahedra. In the $[\text{AlO}_6]$ groups Al^{3+} , on the other hand, is readily replaced by Fe^{3+} and Cr^{3+} . These two cases of diadochic replacement are very common in minerals, and they characterize the geochemistry of iron and chromium. However, no chromium is found in the feldspars and other minerals in which aluminum replaces silicon within the oxygen tetrahedra. It should

also be noticed that, in spite of the valence differences, chromium evidently replaces ferrous iron and magnesium in many minerals.

CYCLE OF CHROMIUM

Because chromium closely resembles ferric iron and aluminum in its chemical properties, ionic size, and ionic charge, it follows these ions during its exogenic cycle. Only very little chromium remains in solutions formed during weathering. Consequently, the precipitates, oxides, and evaporates are nearly completely devoid of chromium, which becomes enriched in the resistates and particularly in the hydrolyzates. The content of chromium in some sediments and sedimentary rocks is presented in Table 28.3.

TABLE 28.3
CONTENT OF CHROMIUM IN SEDIMENTS AND
SEDIMENTARY ROCKS

Rock	Cr (g/ton)
Quartzites, southern Lapland (Sahama, 1945 <i>b</i>)	68-200
Aluminum-rich schists, southern Lapland (Sahama, 1945 <i>b</i>)	410-680
Carbonate rocks, southern Lapland (Sahama, 1945 <i>b</i>)	2
Phyllites, Stavanger area, Norway (O. R��er in Goldschmidt, 1937 <i>b</i>)	140
Bog ores, Finland (Landergren, 1948)	<10
Oolitic siliceous marine iron ores (Landergren, 1948)	240
Marine siderite ores (Landergren, 1948)	20
Lateritic iron ores, northern Ireland (Landergren, 1948)	400

Sahama's values in Table 28.3 show that the distribution of chromium between resistates and hydrolyzates is not very pronounced. This is due to the fact that the chromium present in the femic constituents of rocks, such as pyroxenes, amphiboles, and biotite, is released during the weathering, whereas the chromium present in the oxides chromite, magnetite, and ilmenite is concentrated in the resistates, together with aluminum and ferric iron, because the minerals mentioned are highly resistant to weathering. It is evident that the chromium content of the resistates is largely caused by the presence of chromite. As much as 2,500 g/ton Cr are reported in bauxite.

During metamorphism, the chromium-rich weathering products may give rise to local formation of fuchsite.

In some exceptional cases, when the redox potential is very high, chromium becomes mobilized as chromate because of the oxidation of Cr^{3+} to Cr^{6+} . This is the reason for the presence of notable quantities of chromates in the Chilean nitrate deposits. In this respect chromium resembles vanadium in its exogenic cycle.

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CHROMIUM ORES

It is evident by what is stated in the foregoing paragraphs that only one chromiferous mineral is used as a chromium ore, viz., chromite. This mineral may contain as much as 68 per cent Cr_2O_3 and is mined from ultrabasic rocks in which it occurs as the earliest product of crystallization.

BIOGEOCHEMISTRY OF CHROMIUM

The presence of chromium has been reported in plants and many terrestrial and marine animals. However, in some instances the data may be open to question, owing to the possible contamination of the samples and to analyzing techniques. Therefore, the biological occurrence of chromium cannot be considered fully established in all respects.

Chromium is reported in soil in a content varying from 10 to 5,000 g/ton (Mitchell, 1944). According to Goldschmidt and Peters (1933c), chromium is notably enriched in coal ashes, which may contain as much as 1,000 g/ton Cr.

MOLYBDENUM, TUNGSTEN

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE abundance of molybdenum and tungsten in the meteorites and igneous rocks is presented in Table 29.1. The two metals have also been quantitatively determined in the Sun's atmosphere. With reference to their terrestrial abundance, considerable divergence prevails in the opinions of the various authorities. It seems to be evident that the early abundance values reported by Hevesy and Hobbie (1933) are too high. These authors analyzed a composite

TABLE 29.1
ABUNDANCE OF MOLYBDENUM AND TUNGSTEN

Material	Mo (g/ton)	W (g/ton)
Nickel-iron phase of meteorites (Noddack and Noddack, 1930) .	16 6	8 1
Troilite phase of meteorites (Noddack and Noddack, 1931a)	11	trace
Silicate phase of meteorites (Noddack and Noddack, 1930). . . .	2 5	18
Igneous rocks (Hevesy and Hobbie, 1933)	15	69
Igneous rocks (Mo: Sandell and Goldich, 1943; W: Sandell, 1946).	2 5	1 5
Igneous rocks (Lundegårdh, 1946)		8

mixture of a large number of Caledonian and Variscan igneous rocks from central European localities. Tungsten, at least, is regional in its occurrence; Bjørlykke (1936) has established the presence of pronounced regional differences in its manner of occurrence in Norwegian granite pegmatites. The abundance values given for tungsten by Lundegårdh (1946) and Sandell (1946) are lower than the value obtained by Hevesy and Hobbie (1933). According to Sandell, the most probable value is 1 or 1.5 g/ton. This opinion is shared also by Landergrén (1948) on the basis of the results obtained by analyzing pre-Cambrian rocks of Sweden. It is evident that all abundance values given in Table 29.1 are only tentative.

Figure 2.2 shows that the cosmic abundance of tungsten is somewhat higher than that of molybdenum. In spite of the fact that the

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two metals, according to their positions in the Periodic System, are closely related to each other and also that their chemical properties are much alike, they show notable differences in their geochemical behavior. In the meteorites the highest molybdenum content is found in the metal phase, and a submaximum is present in the sulfide phase, whereas tungsten is strongly concentrated in the silicate phase. The general geochemical character of molybdenum is evidently siderophile, with a definite chalcophile tendency. Tungsten, on the other hand, is strongly lithophile and also shows a weak siderophile bent, but no chalcophile behavior at all.

TABLE 29.2
CONTENT OF MOLYBDENUM AND TUNGSTEN IN IGNEOUS ROCKS

Rock	Mo (g/ton)
Gabbros and norites (Hevesy and Hobbie, 1933)	3
Subsilicic rocks, average (Sandell and Goldich, 1943) . .	2
Granite, Schwarzwald, Germany (Hevesy and Hobbie, 1933)	12
Silicic rocks, average (Sandell and Goldich, 1943)	2 5
Rock	W (g/ton)
Gabbros and norites (Hevesy and Hobbie, 1933)	24
Basic rocks, central Roslagen, Sweden (Lundegårdh, 1946)	10
Silicic and intermediate igneous rocks (Sandell, 1946) . .	1 5
Granite, Schwarzwald, Germany (Hevesy and Hobbie, 1933)	83
Acidic rocks, central Roslagen, Sweden (Lundegårdh, 1946)	7

MOLYBDENUM AND TUNGSTEN IN IGNEOUS ROCKS

In the upper lithosphere both molybdenum and tungsten are oxyphile (see chap. 5). They share the property of becoming pronouncedly concentrated in the last differentiates during magmatic crystallization. The early magmatic nickeliferous sulfide ores contain molybdenum and tungsten in low concentrations. Magmatic sulfides contain, on an average, 20 g/ton Mo and 2 g/ton W (Noddack and Noddack, 1931a). According to Landergren (1948), titaniferous iron ores are low in molybdenum and tungsten (less than 50 g/ton Mo and less than 100 g/ton W). Basic igneous rocks in both the calc-alkalic and the alkalic series regularly contain much less molybdenum and tungsten than do acidic rocks, particularly granites. As a rule, tungsten remains longer in the residual melt than molybdenum does; however, according to Sandell (1946), the concentration of tungsten in silicic rocks does not appear very striking. Considerable amounts

of molybdenum are often met in granites, which conclude the main stage of crystallization, usually in the form of the sulfide molybdenite, MoS_2 , which may form deposits of technical importance. In the granite pegmatites molybdenum and tungsten form a number of independent minerals. The tungsten minerals, in particular, are characteristic of pneumatolytic and hydrothermal deposits. Commercial amounts of molybdenite may also be present in granite pegmatites. Molybdenite is the only sulfide found with any consistency in pegmatites (Landes, 1937). The cassiterite ores carry tungsten as a regular constituent, and in some cases it may even predominate over tin.

Table 29.2 shows the content of molybdenum and tungsten in igneous rocks. It is evident that the number of analyses available is too small to allow any conclusions concerning the detailed distribution of these metals in the various rock classes.

The high affinity of molybdenum for sulfur is illustrated by the fact that it readily collects all sulfur available, to form molybdenite. In the presence of a considerable content of molybdenum during the crystallization, sulfides of other metals may be formed only if there is still sulfur available after the formation of molybdenite. Tungsten also forms the sulfide tungstenite, WS_2 , but it is rare and without geochemical importance. Tungsten is preferentially present in rocks as tungstates. The more important minerals of molybdenum and tungsten include the following species:

Molybdenite,	MoS_2
Powellite,	$\text{Ca}[\text{MoO}_4]$
Wulfenite,	$\text{Pb}[\text{MoO}_4]$
Chillagite,	$\text{Pb}[(\text{Mo}, \text{W})\text{O}_4]$
Scheelite,	$\text{Ca}[\text{WO}_4]$
Stolzite and raspite,	$\text{Pb}[\text{WO}_4]$
Ferberite,	$\text{Fe}[\text{WO}_4]$
Hübnerite,	$\text{Mn}[\text{WO}_4]$
Wolframite,	$(\text{Fe}, \text{Mn})[\text{WO}_4]$

Wolframite is the isomorphic mixture of ferberite and hübnerite and is much more common than scheelite. Powellite and stolzite are the rarest among the above-mentioned minerals. A number of other molybdates and tungstates are known as minerals, containing copper, bismuth, and ferric iron, but are relatively rare and occur as oxidation and alteration products of the common molybdenum and tungsten minerals. In addition, many pegmatite minerals of the rare-earth metals and of columbium and tantalum contain varying amounts of tungsten, for example, columbite and tantalite. The WO_3 content of columbite may run as high as 13 per cent.

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In the molybdates and tungstates molybdenum and tungsten form independent $[\text{MoO}_4]$ and $[\text{WO}_4]$ groups. A property distinguishing between these and the corresponding phosphate and sulfate anions is that in molybdates and tungstates the oxygen ions are not found in the corners of regular tetrahedra but form, instead, a polyhedron which may be obtained if a tetrahedron is compressed along the direction of a crystallographic axis. The resulting deformed tetrahedron is therefore intermediate between the regular tetrahedron and the square.

Owing to the lanthanide contraction, the radii of Mo^{4+} and W^{4+} are equal (0.68 kX). Therefore, the two ions are able to replace each other in minerals, e.g., in chillagite, which represents an isomorphic mixture of wulfenite and stolzite. The presence of columbium and tantalum in wolframite is discussed in chapter 26.

BIOGEOCHEMISTRY OF MOLYBDENUM AND TUNGSTEN

Molybdenum is essential for some fungi and probably also effective in the fixation of nitrogen by soil micro-organisms. According to Goldschmidt and Peters (1933c), it is enriched in coal ashes. The maximum content in soil is 2 g/ton (Mitchell, 1944). Organisms are claimed to concentrate molybdenum by a factor of as much as 1,000. Although molybdenum is reported as a widely distributed constituent of organisms, both continental and marine, many of the occurrences may be caused by molybdenum introduced from irrelevant sources during the analysis. The biological function of molybdenum in animals is unknown. It is accumulated in petroleum hydrocarbons, evidently in the form of organometallic compounds.

Tungsten is reported as a constituent of some marine animals, but its biological functions are almost entirely unknown.

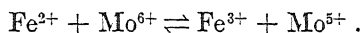
CYCLE OF MOLYBDENUM AND TUNGSTEN

The tungstate minerals are rather stable against mechanical disintegration, whereas the molybdates share this property to a much smaller degree. The minerals of molybdenum and tungsten dissolve readily during weathering and form oxides (ochers) and hydrated oxides, e.g., molybdite, MoO_3 or $\text{FeO} \cdot 3\text{MoO}_3 \cdot 8\text{H}_2\text{O}$; ilsemannite (molybdenum blue), $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O} \pm \text{H}_2\text{SO}_4$; tungstite, WO_3 , partly $\text{WO}_2(\text{OH})_2$; russellite, $(\text{Bi}_2, \text{W})\text{O}_3$; and thorotungstite, a thorium-bearing tungsten oxide. However, secondary molybdenum and tungsten deposits of economic importance are unknown. The soluble

molybdates and tungstates and the colloidal compounds formed during weathering are transported farther without being redeposited in the zone of cementation to any considerable extent. Typical alluvial deposits of scheelite and wolframite do not exist, and only detrital deposits of these minerals on hill slopes or residual deposits formed in arid regions are known to occur.

The sulfuric acid formed during the weathering of sulfides attacks tungstate minerals. Scheelite is decomposed more readily than wolframite is. Calcium, ferrous, and manganous sulfates result from the decomposition of the tungstate minerals under the presence of sulfuric acid. Hydrated tungstic oxide often remains in the weathering zone of tungsten ores. In the presence of alkali carbonates the tungstic oxide goes into solution as an alkali tungstate, and, when tungstate-bearing ground waters react with calcium salts, secondary scheelite may be precipitated.

Ilsemaninite is of widespread occurrence as an oxidation product of molybdenum minerals. Ščerbina (1939) has investigated the reaction



Ilsemaninite is formed when the concentration of ferrous iron is low and that of molybdate is high. On the other hand, the presence of large quantities of ferric iron and a low concentration of molybdate explains the presence of inclusions of wulfenite in siderite. According to Zies (1929), molybdenum blue is readily formed when alkali molybdates in solution come into contact with hydrogen sulfide. In the Valley of Ten Thousand Smokes in Alaska large amounts of molybdenum as ilsemaninite were derived from a rhyolite magma. Ilsemaninite also occurs in the carnotite-bearing sandstones of Utah and Colorado in the United States, being rather plentiful in many places.

When the weathering solutions carrying alkali molybdates and tungstates mingle with river waters rich in calcium, the insoluble calcium salts of molybdic and tungstic acid will be precipitated. If the molybdenum-bearing solutions are brought into contact with reducing sediments, like the muds and sapropelites in lakes and shallow seas, the hydrogen sulfide, which is often present in these surroundings, will precipitate molybdenum as sulfide. The shungites and shungite schists in eastern Fennoscandia contain up to 50 g/ton MoO_3 and 100 g/ton WO_3 , according to Sudovikov (1937) and

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Rankama (1948a). Other bituminous and sapropelic sediments, e.g., the geologically much younger *Kupferschiefer* at Mansfeld in Germany, contain notable amounts of molybdenum as sulfide (140 g/ton Mo).

According to Hauptmann and Balconi (in Goldschmidt, 1937b), molybdenum accumulates especially in manganese-rich oxidate sediments.

Molybdenum and tungsten form stable complex anions with oxygen, and therefore they evidently should be included in Goldschmidt's group of soluble anions with respect to their manner of occurrence in sea water. However, the high calcium content of river waters causes the precipitation of the most part of these metals before they reach the oceans. Consequently, they become incorporated in the hydrolyzates.

The number of determinations of the content of molybdenum and tungsten in sediments and their derivatives is low. According to Landergren (1948), the bog iron ores are low in molybdenum and tungsten. Similarly, their content in iron ores of marine origin is low. In micaceous hematites, Landergren found 300–4,000 g/ton W and in a hematite from Elba 100 g/ton W, but in these minerals the high content may be caused by pneumatolytic activity. Wilson and Fieldes (1944) found an average of 1–2 g/ton W in schists.

Manganese minerals may be rich in tungsten, e.g., 0.63 per cent WO_3 is reported in hollandite and up to 7 per cent WO_3 in psilomelane. The cause of the enrichment is probably the adsorption of colloidal tungsten compounds during the formation of manganese minerals.

MOLYBDENUM AND TUNGSTEN ORES

The ores of the two metals occur regularly in connection with granitic magmas. Molybdenum and tungsten deposits are found in pegmatites and in pneumatolytic and hydrothermal rocks. Molybdenum is also present in ores of other metals, especially in iron ores. Landergren (1948) reported as much as 5,000 g/ton Mo and 1,000 g/ton W in some iron ores from central Sweden. During the metallurgical treatment of such ores, molybdenum goes into both pig iron and slag. Blast-furnace slag may contain as much as 28 per cent Mo. Molybdenum is also recovered as a by-product from the residues of copper smelting.

The only molybdenum minerals of technical importance are

MOLYBDENUM, TUNGSTEN

molybdenite (with approximately 60 per cent Mo) and wulfenite (about 25 per cent Mo), the former being the more important of the two. Wolframite, scheelite, and tungstite are important as tungsten ores. Both ferberite and hübnerite contain, when pure, about 60.5 per cent W, whereas the content in scheelite is a little higher, or 63.9 per cent W. The greatest and most important tungsten deposits consist of wolframite. China leads the world as a tungsten producer; the most important deposits are located in the southern Kiangsi Province.

URANIUM

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

URANIUM was previously included in the same group of the Periodic System in which chromium, molybdenum, and tungsten are contained. However, if the manner of occurrence of these elements is considered, uranium is found to depart much from the others. The recent results of nuclear research have established the presence of an actinide series in the Periodic System. This series begins with actinium and corresponds closely to the lanthanides. The presence of a series resembling the rare-earth metals was predicted by Niels Bohr as early as 1922. The various actinides resemble one another noticeably. Their ionic sizes afford proof of the presence of an actinide contraction, which is similar in its effects to the lanthanide contraction (chap. 5). Thus, for example, the radius of Th^{4+} is 1.10 kX, whereas that of U^{4+} is 1.05 kX. Because of the similarity of their ionic sizes, uranium and thorium accompany each other in Nature.

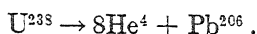
Geochemically, uranium is a pronouncedly lithophile element. Its abundance values are given in the accompanying tabulation. There

Material	U (g/ton)
Iron meteorites (Arrol, Jacobi, and Paneth, 1942) . . .	0.007
Silicate meteorites (Hevesy, Alexander, and Wüstlin, 1930)	0.4
Igneous rocks (Hevesy, 1932)	4
Upper lithosphere (Tomkeieff, 1946)	1

are no abundance values to show the content of uranium in the sulfide phase of the meteorites. Its presence in the solar atmosphere is still unsettled.

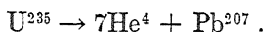
Uranium and all its compounds are radioactive. This property was discovered by the French physicist, Henri Becquerel, in 1896. Uranium is found in Nature as three semistable isotopes: U^{234} , U^{235} , and U^{238} , the last one being the most abundant of them all (99.28 per

cent). Radium is formed as one of the intermediate products during the decay of U^{238} or UI (see chap. 46). This uranium isotope is the ancestor of a series of radioactive elements, called the uranium-radium family. A total of eight α -particles and six β -particles is emitted during the continued disintegration of U^{238} , and the lead isotope Pb^{206} (RaG) is the final stable atom obtained:



The half-life of U^{238} is about $4.5 \cdot 10^9$ years.

The less abundant (0.71 per cent) uranium isotope U^{235} (AcU) heads another series of genetically related radioactive elements (the uranium-actinium family). The half-life of the parent-isotope is $8.8 \cdot 10^8$ years. It emits a total of seven α -particles and four β -particles, and the lead isotope Pb^{207} (AcD) is the stable end-product of its disintegration:



The two lead isotopes formed in the uranium disintegration accumulate in the uraniferous minerals.

The presence of natural fission in uranium has been established; uraninite contains a trace of plutonium (see chap. 46).

URANIUM IN IGNEOUS ROCKS

Like thorium, uranium is a pronouncedly oxyphile element. It never occurs in the native state and does not form sulfides, arsenides, tellurides, etc. The association U-S is known only in the hydrous uranium sulfates. Uranium is strongly concentrated in the upper lithosphere, which is illustrated by the calculations made of the radioactivity of rocks and of its significance in the generation of heat in the lithosphere. Along with uranium and thorium, the short-lived radioactive elements (see chap. 46) and the following nuclides are radioactive: K^{40} , Rb^{87} , La^{138} , Sm^{152} , Lu^{176} , and Re^{187} . The five last mentioned nuclides, owing to their scarcity, have no considerable effect on the amount of radioactive heat generated in the Earth's crust. On the other hand, much heat is produced by the radioactive disintegration of uranium, thorium, and potassium. The calculations show that even a relatively thin superficial layer of the Earth, corresponding in thickness to the Sial crust and containing the above three radioactive elements in concentrations given in Table 2.3, is able to produce heat enough to compensate for the loss of heat by radiation into interplanetary space. Therefore, it is evident that only negligible amounts

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of the radioactive elements can be present in the Sima layer, to say nothing about their concentration in the deeper geospheres. Further proof of this assumption is furnished by the observation that during magmatic differentiation these elements become strongly concentrated in acidic rocks. The average contents in the various groups of igneous rocks which are considered the most reliable ones are given in Table 30.1. The values show that granites, among all igneous rocks of the calc-alkalic series, are the richest in uranium. According to Senftle and Keevil (1947), the Th/U ratio in acidic igneous rocks is 3.4, and in intermediary igneous rocks it is 4.0. These values are based on very extensive material. They show that, during crystallization, uranium becomes enriched in the acidic rocks with regard to thorium.

TABLE 30.1
ABUNDANCE OF URANIUM IN IGNEOUS ROCKS

Rock	U (g/ton)
Basic igneous rocks (Evans and Goodman, 1941)	0.96
Basalts (Evans and Goodman, 1941)	0.83
Diabases (Evans and Goodman, 1941)	0.83
Intermediary igneous rocks (Senftle and Keevil, 1947)	2.61
Granitic rocks (Senftle and Keevil, 1947)	3.963

During the differentiation, uranium is often already concentrated in granite and syenite pegmatites, in which it may form a number of independent minerals. The radius of the U^{4+} ion is too great to allow the admission of material amounts of uranium in the common rock-making minerals. Although the U^{4+} ion, like the Th^{4+} ion, resembles Ca^{2+} in co-ordination, it becomes enriched in residual solutions, notwithstanding its E -value (Wickman, 1943). In this respect, uranium also resembles the rare-earth metals.

The minerals crystallized at elevated temperatures contain relatively much UO_2 , which may be assumed to be of primary origin. All minerals of low-temperature assemblages contain only UO_3 , which is an oxidation product (Tomkeieff, 1946). In pegmatites the early-crystallizing minerals, such as columbates and tantalates, are low in uranium; the uranium-rich minerals are formed during the late stages of deposition.

During the pneumatolytic and hydrothermal stages uranium occurs in high-temperature hydrothermal tin veins associated with sulfides and sulfosalts containing cobalt, nickel, bismuth, and arsenic. Hydrothermal sulfide and arsenide veins carrying cobalt, nickel,

silver, and bismuth minerals and formed at low temperatures and similar veins devoid of cobalt and nickel are also uraniferous. In silicate rocks uranium may accompany zirconium and thorium in zircon, as well as thorium and the rare-earth metals in their minerals, e.g., in thorite, thorianite, monazite, xenotime, and allanite. In pegmatites, uranium, however, prefers the company of titanium, columbium, and tantalum, and many columbates and tantalates found in such rocks are uraniferous. Carbonaceous material (thucholite) often accompanies uranium in pegmatites, probably resulting from the radioactive polymerization of hydrocarbons.

The most important uranium mineral is the oxide, UO_2 , found as uraninite and pitchblende. These minerals show wide variations in their composition. The crystallized uraninite is almost entirely confined to pegmatites, whereas the hydrothermal sulfide and arsenide veins nearly always carry the massive pitchblende. Uraninite is the richest of all uranium minerals and may contain 75–90 per cent UO_2 and UO_3 . A number of other independent uranium minerals is known; they are hydroxides, phosphates, arsenates, vanadates, uranates, carbonates, silicates, and sulfates of variable and often complicated chemical composition. They are usually derived from the alteration or decomposition of primary uranium minerals, notably uraninite. These minerals are particularly numerous in hydrothermal veins and may occur in both igneous and sedimentary rocks. Many of them are found in the weathered parts of uraniferous ore bodies, e.g., becquerelite, $2\text{UO}_3 \cdot 3\text{H}_2\text{O}$. The vanadate, phosphate, and arsenate minerals of uranium contain UO_2 layers alternating with $[\text{PO}_4]$, $[\text{AsO}_4]$, and $[\text{VO}_4]$ layers in the structures. Therefore, they are structurally similar to the micas and are, accordingly, called uranmicas (uranite group). The most important minerals of this group are carnotite, perhaps $\text{K}[\text{UO}_2|\text{VO}_4] \cdot 1\frac{1}{2}\text{H}_2\text{O}$; torbernite, $\text{Cu}[\text{UO}_2|\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$; and autunite, $\text{Ca}[\text{UO}_2|\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$. Kasolite, $\text{PbU}[\text{O}_2|\text{SiO}_4] \cdot \text{H}_2\text{O}$, and uranophane (uranotil), $\text{CaU}_2[(\text{OH})_3|\text{SiO}_4]_2 \cdot 4\text{H}_2\text{O}$ (?) are here mentioned as representatives of uranium silicates. Uranium may also be incorporated in late hydrothermal minerals, e.g., in fluorite and opal; in the latter mineral it may be present as a uranyl silicate or phosphate (Haberlandt and Hernegger, 1947).

The pegmatitic and pneumatolytic-hydrothermal enrichment of uranium is characteristic of its geochemistry. Another peculiarity in the manner of occurrence of uranium is its concentration, notably in the company of vanadium, in minerals precipitated from ground

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waters in arid regions. Such uranium deposits are sometimes found in sandstones.

CYCLE OF URANIUM

During weathering, the uranium minerals yield hydrated uranium oxides, which are sparingly soluble. Some uranium remains in the highly resistant minerals and may become concentrated in placers. Only a small part of uranium goes into solution, preferably as the readily soluble uranyl complexes, which are understood as basic salts containing U^{3+} and UO_3 . The alkali uranates are only sparingly soluble. The soluble uranium compounds are readily adsorbed on the

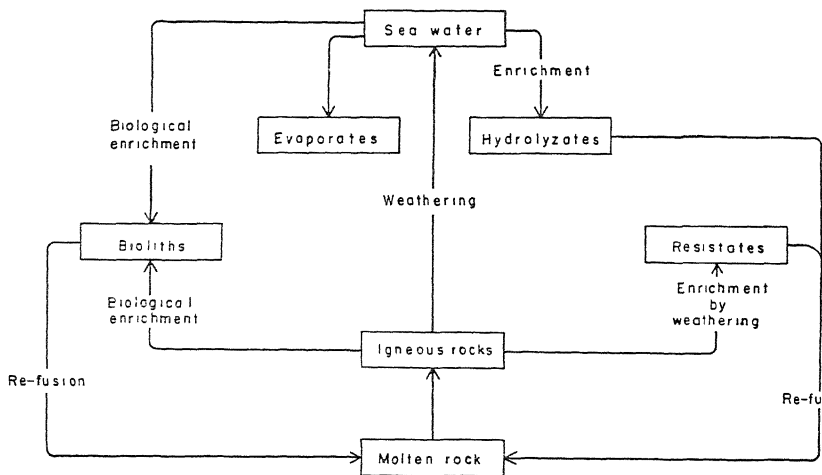


FIG. 30.1.—The cycle of uranium

hydroxide gels of iron, aluminum, and manganese, and on silica gel, and therefore uranium may become enriched in hydrolyzates and oxidates. This property of uranium is evidently one of the general causes of its dispersed manner of occurrence. A part of uranium remains in sea water and is finally deposited in marine evaporates. The cycle of uranium is shown in Figure 30.1.

The terrigenous sediments are often rather rich in uranium, the reason being the presence of detrital heavy minerals therein. The determinations of the uranium content in sediments and sedimentary rocks are few. Urry (1941) found 0.65–1.07 g/ton U in some marine sediments, and Evans and Goodman (1941) reported the average of 1.3 g/ton U in limestones and 1.2 g/ton U in other sedimentary rocks than limestones. These values show that the enrichment of uranium is negligible in sediments devoid of organic material.

BIOGEOCHEMISTRY OF URANIUM

Uranium occurs in many organisms; it may have a definite physiological function and probably is an element essential for the life-processes. The following contents are reported by v. Thyssen-Bornemisza (1942): about 0.005 g/ton U in humus soil and in coal ashes and up to 7 g/ton in plant ashes. Uranium is concentrated in many terrestrial and marine organisms, and it is possible that the cause of enrichment is the adsorption of uranium compounds by biological substances. An unusually high concentration of uranium occurs in the thyroid. Föyn, Karlik, Pettersson, and Rona (1939) found more uranium in the deep ocean waters than in the surface water, and Pettersson (1939) explained this observation by assuming that uranium might be enriched by the plankton organisms in the surface layers of the sea. Sediments deposited by hot springs may contain uranium, which is believed to be sometimes precipitated by bacteria. It is also known that algae growing in fresh water accumulate uranium.

Carbonaceous shales of marine origin are very definitely higher in uranium than are other sedimentary rocks and even granites. It is believed that uranium sometimes is precipitated as sulfide, together with iron, in the original sapropelic sediments, and sometimes together with vanadium, molybdenum, and nickel. Beers and Goodman (1944) found that the contents of potassium and uranium increase directly with each other in organogenic black shales and also in igneous rocks.

So far, no uranium has been detected in the normal *Kupferschiefer* of Mansfeld in Germany (Kohl, 1941). The uraninite present in the Mansfeld ores may have been deposited from highly concentrated and mineralized brines, partly of connate origin and partly mixed with ascending juvenile waters.

A famous example of the enrichment of uranium in coal is kolm, the ash-rich coal found in alum shales in Sweden. Eklund (1946) reports a maximum of more than 1 per cent U in kolm. The kolm-bearing alum shales of southern Sweden usually contain about 200 g/ton U, but in the bulk of these shales the content is 50–100 g/ton.

Petroleum and associated brines are always rich in uranium. Tomkeieff (1946) quotes 100 g/ton U as the average content in petroleum. In oil-field waters the content is 10 g/ton U. Uranium is also reported in asphaltiferous sandstones and asphaltites. An asphaltite from Utah, in the United States, is stated to contain 2.88 per cent uranium.

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The most important feature of the biogeochemistry of uranium is its enrichment in sedimentary rocks as a result of biological processes. Uranium is, in addition, very often closely associated with vanadium in the bioliths.

ORES OF URANIUM

Uranium is produced partly from deposits found in sedimentary rocks, particularly in sandstones and bituminous shales containing uranites, especially carnotite. However, the most important uranium ores are uraninite and its alteration products found in hydrothermal deposits. Small amounts of uranium minerals are common in pegmatites, but they are usually without technical significance. A most notable feature in the regional geochemistry of uranium is the very limited number of rich uranium deposits. The greatest and most important uraninite ores are found in the vicinity of the Great Bear Lake in Canada, in Katanga in the Belgian Congo in West Africa, and in Jáchymov (Joachimstal) in Czechoslovakia. They are all associated with hydrothermal veins. The carnotite deposits in vanadiferous sandstones in southeastern Utah and southwestern Colorado in the United States are believed to be secondary. They may have been derived by precipitation from ground waters rich in uranium salts leached from primary uraninite deposits in granitic rocks. Some of the deposits are associated with plant remains, and therefore a biological enrichment of uranium would also be possible. Carnotite deposits also occur in Fergana in Russia (central Asia). In these deposits the presence of the mineral tyuyamunite, $\text{Ca}[\text{UO}_2|\text{VO}_4]_2 \cdot 4\text{H}_2\text{O}$, is explained as a result of extraction of uranium and vanadium from neighboring bituminous shales containing, on an average, approximately 400 g/ton U and 850 g/ton V. Large amounts of uranium and thorium have been produced from the aforementioned deposits alone. Nowhere else does uranium seem to occur in concentrations high enough to make industrial operations normally profitable. No noteworthy uranium deposits are known in the pre-Cambrian areas of Fennoscandia, although they are geologically comparable with the Canadian Shield. However, the much younger kolm and alum shales of Sweden and Estonia are potential sources of uranium.

The position occupied by uranium in the Periodic Table is responsible for the comparatively large size of the quadripesitive uranium ion. In addition, uranium may change its ionic charge comparatively readily according to the circumstances prevailing in its surroundings.

Further, the strong radioactivity of the uranium atom causes the decomposition of the structures of all minerals containing uranium in noteworthy amounts, whereby structurally anisotropic or metamict minerals are produced. All these properties of uranium are responsible for the fact that it will not become enriched in mineral structures so easily as many other elements do. Another result is that uranium is not very much inclined to form rich ore bodies. Consequently, uranium may, to some extent, be considered one of the dispersed elements in the sense of Vernadsky (1924), even though its dispersion is not so complete and far-reaching as that of, e.g., bromine and iodine.

MANGANESE

ABUNDANCE AND GEOCHEMICAL CHARACTER

MANGANESE is, next to titanium, the most abundant among the trace elements found in igneous rocks. Owing to the rather easy quantitative determination even of small traces of manganese in minerals and rocks by colorimetric methods of analysis, it is usually included in the list of constituents determined during the course of rock and mineral analyses made for petrological purposes. The number of manganese determinations available is great enough to

TABLE 31.1
ABUNDANCE OF MANGANESE

Material	Mn (g/ton)
Meteoritic irons (Noddack and Noddack, 1930)	300
Troilites (Noddack and Noddack, 1930)	460
Silicate meteorites (Merrill, 1916; recalculated by Goldschmidt, 1937b)	2,600
Igneous rocks (Clarke and Washington, 1924; Hevesy, Merkel, and Würstlin, 1934)	1,000
Igneous rocks, Dutch East Indies, average (van Ton- geren, 1938)	2,200

make this metal rather well known as far as its geochemistry in the upper lithosphere is considered. The abundance values of manganese are presented in Table 31.1.

Manganese is geochemically a strongly lithophile metal. It is concentrated in the silicate phase of the meteorites and in the lithosphere. In the upper lithosphere manganese is oxyphile. It is not siderophile but has some chalcophile tendency, which is illustrated by its behavior in metallurgical processes (see Table 4.1). In the meteorites the chalcophile character of manganese is distinct, as its presence in oldhamite shows. According to Goldschmidt (1937b), the ratio between the manganese content of the silicate and metal phases of the meteorites is approximately 9:1. The average content of manganese in the troilite nodules is somewhat higher than the content in the

metal phase. In the solar atmosphere the abundance of manganese is relatively high.

The abundance value calculated by van Tongeren (1938) probably means that there are regional differences in the manganese content of the upper lithosphere.

With reference to its terrestrial occurrence, manganese also possesses a distinct biophile tendency.

MANGANESE MINERALS

Manganese is related to iron in its chemical properties and is a member of the iron family (Goldschmidt, 1929) or the ferrides (Landergren, 1943). In the Periodic System manganese occurs next to the Fe-Co-Ni triad. Actually, it resembles iron in many respects as far as its manner of occurrence in Nature is concerned. However, there are also important fundamental differences between the two metals in this respect. Like chromium, manganese forms a number of independent minerals in igneous rocks, but usually they are rare and geochemically insignificant. Nearly all mineral groups of petrological importance contain a manganese constituent, which is sometimes found as an independent mineral.

In artificial silicate melts, manganese forms the simple metasilicate, the corresponding simple orthosilicate, and the compound $3\text{MnO} \cdot 2\text{SiO}_2$. The orthosilicate or the manganolivine is found in Nature as the rare tephroite, $\text{Mn}_2[\text{SiO}_4]$, which contains 70.25 per cent Mn. Tephroite also forms isomorphic mixtures with fayalite, known as manganfayalite and knebelite, $(\text{Mn},\text{Fe})_2[\text{SiO}_4]$. The metasilicate is known, e.g., as rhodonite, $(\text{Mn},\text{Fe},\text{Ca})[\text{SiO}_3]$, and pyroxmangite, $(\text{Mn},\text{Fe})[\text{SiO}_3]$, which were previously considered members of the pyroxene group. However, their structures differ from that of the pyroxenes, and it is probable that they contain $[\text{Si}_3\text{O}_9]$ rings. The manganese silicates with more complicated composition include the manganese garnet spessartite, $\text{Mn}_3\text{Al}_2[\text{SiO}_4]_3$, with 15–40 per cent MnO; manganepidote; ardennite, a member of the zoisite group; manganhedenbergite; the manganese-bearing micas alurgite, manganphlogopite (with up to 18 per cent MnO), and manganophyllite (maximum 18 per cent MnO); manganchlorite; and still others. Helvite, $\text{Mn}_8[\text{S}_2](\text{BeSiO}_4)_6$, is a mineralogical curiosity, with the probable exception of the locality at Iron Mountain in New Mexico in the United States (Glass, Jahns, and Stevens, 1944).

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Among the manganese oxides and hydroxides the following minerals are the most important:

Galaxite (manganspinel),	MnAl_2O_4
Jacobsite (manganspinel),	MnFe_2O_4
Manganosite,	MnO
Hausmannite,	Mn_3O_4 (72 per cent Mn)
Braunite, $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$; perhaps $(\text{Mn},\text{Si})_2\text{O}_3$	(71.5 per cent Mn)
Pyrophanite (manganilmenite),	MnTiO_3
Pyrolusite (polianite),	MnO_2 (60–63 per cent Mn)
Manganomelane,	MnO_2 (about 58 per cent Mn)
Pyrochroite and bäckströmite,	$\text{Mn}(\text{OH})_2$
Manganite,	MnOOH (69 per cent Mn)

Manganomelane consists of a series of, in part, amorphous minerals (psilomelane, wad, cryptomelane), partly with adsorbed accessory elements (see under "Cycle of Manganese," p. 650). Pyrolusite, manganomelane, and braunite are the most common oxide and hydroxide minerals of manganese. Manganosite and pyrochroite (bäckströmite) have no counterparts among the iron minerals. They are rather unstable. Pyrophanite, like geikielite, MgTiO_3 , is very rare.

In its independent silicate minerals, manganese occurs nearly exclusively in the form of Mn^{2+} ions. In its oxides, manganese, however, is often present as Mn^{3+} ions and still more commonly as Mn^{4+} ions.

Rhodochrosite, MnCO_3 , with 61.7 per cent Mn, is the most important among the carbonate minerals of manganese. Among other manganese minerals containing complex anions, the following species are rich in manganese: wolframite (with 5–15 per cent MnO) and particularly hübnerite, $\text{Mn}[\text{WO}_4]$; triphylite and lithiophilite, $\text{Li}(\text{Mn}^{2+}, \text{Fe}^{2+})[\text{PO}_4]$; and triplite, $(\text{Fe}^{2+}, \text{Mn}^{2+})_2[\text{F}|\text{PO}_4]$. There are also chloride, arsenite, arsenate, antimonate, vanadate, borate, and sulfate minerals of manganese, such as scacchite, MnCl_2 ; trigonite, $\text{Pb}_3\text{MnH}[\text{AsO}_3]_3$; sussexite, MnHBO_3 ; sarkinite, $\text{Mn}[\text{OH}|\text{AsO}_4]$; pyrobelonite, $\text{PbMn}[\text{OH}|\text{VO}_4]$; and mallardite, $\text{Mn}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$.

The manganese sulfide alabandite, $\alpha\text{-MnS}$, contains 63.2 per cent Mn. It belongs structurally to the galena type. Alabandite is found in some hydrothermal veins. In the meteorites the manganese sulfide forms isomorphic mixtures with oldhamite, CaS , and a corresponding calcium-manganese sulfide may be present also in metallurgical slags. Another manganese sulfide is hauerite, MnS_2 , which is isotypic with pyrite and rather rare.

MANGANESE IN IGNEOUS ROCKS

The manganese minerals mentioned in the previous paragraph are only seldom found as primary constituents of igneous rocks formed during the main stage of crystallization. They are generally constituents of metamorphic and sedimentary rocks. The reason for this manner of occurrence is that during the formation of igneous rocks manganese usually, during the main stage of crystallization, does not become enriched enough to be able to form independent minerals. Such minerals are formed only when the manganese content of the melt is exceptionally high. By far the greatest part of the manganese present in igneous rocks is concealed in the structures of other rock-making

TABLE 31.2
CONTENT OF MnO AND FeO AND THE MnO:FeO
RATIO IN IGNEOUS ROCKS

Rock	MnO	FeO	MnO:FeO
	Per Cent		
Gabbro	0.15	8.6	0.017
Diorite	0.09	6.0	0.015
Granite	0.05	2.9	0.018
Granite pegmatite			1

minerals. This manner of occurrence is one of the features characterizing the geochemistry of manganese.

In igneous rocks manganese, in the first place, accompanies iron. The average chemical composition of the various classes of igneous rocks calculated by Daly (1933; see Table 5.32) shows that the content of manganese is rather stable, and a higher content is present only in the ultrabasics, such as dunites and hornblendites. The manganese and iron content and the MnO:FeO ratios in some groups of igneous rocks are presented in Table 31.2, which is based on a paper of Otto (1936). In addition, the average content of manganese in the various classes of calc-alkalic igneous rocks is presented in Table 31.3, which is based on the analyses published by Hevesy, Merkel, and Würstlin (1934).

The values presented in Tables 31.2 and 31.3 show that the MnO:FeO ratio in rocks formed during the main stage of crystallization is very stable and that the manganese content of silicic rocks is somewhat lower than that of subsilicic rocks. However, the content

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of ferrous iron also decreases simultaneously. In its behavior during the magmatic crystallization, manganese differs markedly from chromium, for instance, which is very pronouncedly concentrated in the early crystallates. There is, further, a difference between the behavior of iron and that of manganese which is shown by the notable degree of concentration of manganese in the late magmatic crystallates—pegmatites and pneumatolytic rocks. This difference is caused by the size of the Mn^{2+} ion, which is incorporated in both magnesium and calcium silicates with considerable difficulty. As a result of the concentration of manganese, the $\text{MnO}:\text{FeO}$ ratio increases very strongly in pegmatites (Table 31.2). The change is also illustrated by the values calculated by Goldschmidt (1929) for the $\text{Mn}:\text{Fe}$ ratio in olivines from the early crystallates (about 1:80) and in biotite, the last ferromagnesian silicate to crystallize during the main stage of differentiation (from 1:30 to 1:15).

TABLE 31.3
CONTENT OF MANGANESE IN IGNEOUS ROCKS

Rock	Mn (g/ton)
Peridotites, eclogites, dunites	1,060
Ultrabasic rocks	1,120
Diorites	1,230
Granites	965
Greisen	1,100

As a result of the enrichment in manganese, pegmatites and rocks of pneumatolytic origin often contain a number of oxide, phosphate, and silicate minerals rich in this metal. Along with the phosphates mentioned in the preceding paragraph, there occur in granite pegmatites natrophilite, $\text{Na}(\text{Mn}^{2+}, \text{Fe}^{2+})[\text{PO}_4]$; manganoan columbite and tantalite, with up to 16 per cent MnO ; and other manganese-bearing columbium and tantalum oxides. Spessartite occurs in aplitic granite pegmatites. The wolframites of pneumatolytic tin-tungsten veins are rich in manganese. Hydrothermal veins often carry rhodochrosite or siderite high in manganese (mangansiderite). Manganese is also present in thermal waters, and sometimes it is deposited by hot springs. Hydrothermal solutions, when brought into contact with oxygen-bearing ground waters, may deposit manganese as dioxide.

Astrophyllite, $(\text{K}_2, \text{Na}_2, \text{Ca})(\text{Fe}^{2+}, \text{Mn}^{2+})_4(\text{Ti}, \text{Zr})[\text{OH}|\text{Si}_2\text{O}_7]_2$, with 3.5–12.5 per cent MnO , is found in nepheline syenite pegmatites. Alkalic rocks usually contain more manganese than do the calc-alkalic rocks.

The manner of occurrence of manganese in igneous rocks depends on its ability to replace other cations diadochically. Manganese occurs in three states of oxidation in mineral structures, viz., as bi-, tri-, and quadripesitive ions. The radii of these ions, as compared with those of some other ions, are the following:

Mn^{2+} , 0.91 kX	Mn^{3+} , 0.70 kX	Mn^{4+} , 0.52 kX
Fe^{2+} , 0.83 kX	Fe^{3+} , 0.67 kX	
Mg^{2+} , 0.78 kX	Al^{3+} , 0.57 kX	
Zn^{2+} , 0.83 kX	Cr^{3+} , 0.64 kX	
Ca^{2+} , 1.06 kX		

In igneous rocks manganese is present almost exclusively as Mn^{2+} ions. Because of the low redox potential of natural silicate melts, bivalent manganese is the only state of oxidation of manganese which is stable at temperatures prevailing during the crystallization of such melts. Trivalent manganese, as a rule, is but rarely present in igneous rocks. According to Otto (1936), only some pneumatolytic and hydrothermal minerals contain manganese in this state of oxidation, e.g., manganandalusite and viridine, $(\text{Al,Fe,Mn})_2[\text{O}|\text{SiO}_4]$, in which it replaces ferric iron, aluminum, and, partly, chromium. Quadripesitive manganese is the dominating form in sediments and sedimentary rocks.

The ionic radii listed above show that the bipesitive manganese ion is able to replace diadochically the following ions: Fe^{2+} , Mg^{2+} , Zn^{2+} , and Ca^{2+} . The replacement of Fe^{2+} by Mn^{2+} is the most common and geochemically the most important among the various possibilities.

The dark silicate minerals which contain hydroxyl groups in their structures are the highest in manganese. Thus biotite contains up to 1 per cent MnO and hornblende 0.3 per cent. In general, these chemically and structurally rather complicated minerals tend to collect a number of accessory elements in their structures. High contents of manganese are sometimes reported also in a number of other silicate minerals, e.g., 3 per cent MnO in almandite, 2 in tourmaline, 0.6 in pyrope, 0.4 in augite, and 0.1 in muscovite. In magnetite and ilmenite, the most common opaque constituents of igneous rocks, the average manganese content, however, is decidedly lower, although magnetite is reported to carry sometimes as much as 1.5 per cent MnO.

Along with the Mn^{2+} - Fe^{2+} diadochy, the Mn^{2+} - Mg^{2+} diadochy is also possible, but the degree of the replacement is less complete in this case because the difference of the dimensions of the ions is greater than in the previous instance. Consequently, the magnesium miner-

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als low in iron are low in manganese as well. Another possibility of replacement is the Mn^{2+} - Zn^{2+} diadochy, which, however, is mainly of only mineralogical interest. Manganese is incorporated in sphalerite, and the highest content is found in sphalerites formed at elevated temperatures (Oftedal, 1940). The diadochy between Mn^{2+} and Ca^{2+} , although possible, is geochemically unimportant. It is found in apatites. According to Otto (1936), the manganese content of apatites from the various classes of igneous rocks is as given in the accompanying tabulation. These values show that the apatites found

Source of Apatite	MnO (Per Cent)
Gabbro.....	0.1
Granite	0.3
Granite pegmatite.....	3.4
Syenite	0.2
Nepheline syenite.....	0.2

in granite pegmatites are very rich in manganese, which is another result of the enrichment of manganese in these rocks. According to Haberlandt (1938), pegmatitic and pneumatolytic apatites from residual magmas are extremely rich in manganese and may contain up to 9 per cent MnO. Contrary to the case with apatites, manganese is unable to replace calcium in the feldspars and in the feldspathoids. This is well explained by the thermochemical considerations of Schiebold (1931).

In the series of Fournet and Schütz, which establishes the affinity of the metals for sulfur (see chap. 36), manganese precedes all other metals, iron among them. Although its affinity for sulfur is higher than that of iron, it is not a very conspicuous constituent of magmatic sulfide segregations. According to Noddack and Noddack (1931), the manganese content of primary magmatic sulfides is 800 g/ton. The sulfides alabandite and hauerite are found in mineral veins and do not belong to the early sulfide assemblages separated from rock melts. In addition, pyrite and pyrrhotite, the most common iron sulfides, are usually nearly totally devoid of manganese. Therefore, it may be concluded that the Mn^{2+} - Fe^{2+} diadochy is rather uncommon in sulfide minerals. The absence of manganese in the magmatic sulfide segregations, according to Otto (1936), is due to the fact that the manganese sulfide, MnS , is more readily soluble than is the iron monosulfide, FeS . Therefore, manganese will not become separated as sulfide in noteworthy quantities in spite of its higher affinity for sulfur.

CYCLE OF MANGANESE

During weathering, manganese is dissolved mainly as the bicarbonate, $\text{Mn}(\text{HCO}_3)_2$, and behaves in this respect like iron (see chap. 33). The sulfate, MnSO_4 , is present in weathering solutions only in small quantities. Because the content of manganese in igneous rocks is lower than that of iron, manganese is usually scarcer than iron in the weathering solutions. Actually, manganese is dissolved in carbon dioxide- and sulfate-bearing waters more readily than iron is, and the manganous compounds are more stable in solution than are the ferrous compounds. In carbonate-bearing waters the Mn:Fe ratio is about 5:1 and in sulfate-bearing waters about 1:1. Because of the higher stability of manganous bicarbonate, manganese may, under favorable conditions, become somewhat enriched in the weathering solutions with respect to iron. The decomposition of the bicarbonate leads to the formation of Mn^{4+} compounds. In the zone of weathering the carbonate is directly converted into manganic oxides and hydroxides. In this respect manganese behaves like iron, and the formation of the hydroxides is an important step in the cycle of the two metals. The general rule is that both iron and manganese go into solution at low redox potentials and are precipitated at high ones.

Manganese is most soluble in acid solutions when in the bivalent state. Manganous bicarbonate is stable in solution under reducing circumstances, e.g., when humic compounds are present. Humic complexes are consequently of importance in the transportation of manganese (Aschan, 1932). Bivalent manganese is readily oxidized to the quadrivalent state when the weathering solutions are brought into contact with atmospheric oxygen or dissolved oxygen in lakes or in shallow near-shore waters in the sea. The oxidation may already have taken place in the original weathering solution. The quadrivalent manganese remains first in solution as a colloidal hydroxide, probably stabilized by organic colloids. Under proper circumstances, manganese is precipitated as $\text{Mn}(\text{OH})_4$ or finely divided MnO_2 . The precipitation is nearly quantitative and often takes place in fresh waters. Most of the remaining manganese is removed in brackish water at the river mouths in the sea. Therefore, the content of manganese in sea water is very low. Manganese is also precipitated when carbon dioxide is removed from the bicarbonate by the action of bacteria or by oxidation. Bacteria may also utilize the organic substances acting as protective colloids. In these instances manganese is precipitated

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either as carbonate or as hydroxide. The manganese precipitated by the processes discussed is deposited quantitatively in the oxidate sediments, often in the form of concretions, nodules, and slabs. Its content in the hydrolyzates and precipitates is small and is negligible in the evaporates.

Under reducing conditions the precipitated manganese hydroxide may again pass into solution. The most favorable conditions for a nonreversible precipitation of manganese include oxidizing environments (relatively high redox potential) and the presence of small quantities of solid calcium carbonate (relatively high pH).

In carbonate sediments manganese may become enriched in relation to iron. The cause of the enrichment is the diadochic replacement of Ca^{2+} by Mn^{2+} in calcite, which takes place more readily than the substitution of Ca^{2+} by Fe^{2+} , owing to the smaller difference in the ionic size of the former two metals.

In the deep-sea sediments, manganese as MnCO_3 is rather common, but the bulk is present as the dioxide, MnO_2 . Correns (1941) has suggested that a biological extraction from sea water is responsible for the accumulation of manganese in deep-sea deposits, and Kuenen (1941) advocated chemical precipitation for the same purpose. According to Correns, manganese, like iron, promotes the growth of diatoms, which adsorb it on their surface. Manganese is deposited in the calcareous shells of the foraminifers feeding upon the diatoms, and it replaces calcium diadochically in the calcite structure of the shells. Manganese is enriched in the shells by a factor of about 100,000 (calculated for MnO). When calcium carbonate dissolves from the red clay, manganese becomes enriched in relation to iron because ferric hydroxide remains suspended and may migrate, contrary to manganese, which is more readily precipitated and concentrated. However, Pettersson (1945) emphasized the higher stability of manganese compounds, as compared with those of iron, when dissolved or suspended in sea water. According to Pettersson, the adsorption of manganese on volcanic dust is more important than its biological precipitation with plankton or its inorganic precipitation. The deep-sea manganese cannot, totally or largely, come from sea water. Submarine volcanic eruptions form the main source of manganese deposited on the ocean floor, and this element is released by submarine weathering, which is activated by the generation of hydrochloric acid, which dissolves more manganese than iron from the submarine lavas.

A comparison of the chemical behavior of iron and manganese at different states of oxidation reveals that bivalent manganese, like bivalent iron, does possess relatively strong basic properties and consequently remains in aqueous solution even in the presence of weak and dilute acids, whereas tri- and quadrivalent manganese, in analogy with trivalent iron, are so weakly basic that their compounds are largely or totally hydrolyzed in waters on the Earth's surface. Therefore, the oxidation of bivalent manganese results in the precipitation of quadrivalent manganese as hydroxide in aqueous solution.

The foregoing discussion shows that the cycle of manganese resembles that of iron in its essential features. Manganese, like iron, is enriched in the hydrolyzate residue formed in lateritic weathering. The two metals are concentrated mostly in oxidate sediments. They are nearly totally absent in sediments formed as a result of solution and reprecipitation or crystallization. Their content in sea water is very low.

In oxidate sediments iron and manganese, however, are separated from each other more or less completely. This is partly caused by the fact that the affinity of manganese for oxygen is lower than that of iron. Therefore, iron is readily oxidized to the ferric state and subsequently precipitated as ferric hydroxide, whereas manganese remains in solution until the bulk of the iron is precipitated. The separation of iron and manganese may, however, follow a different course. Ferric hydroxide, $\text{Fe}(\text{OH})_3$, is weakly basic, whereas manganic hydroxide, $\text{Mn}(\text{OH})_4$, has a weakly acid character. Therefore, the $\text{Fe}(\text{OH})_3$ hydrosol is positively charged and the $\text{Mn}(\text{OH})_4$ hydrosol negatively charged. This basic difference in the properties of colloidal ferric and manganic hydroxide is the essential cause of the formation of iron-poor or iron-free manganese deposits. If the two sols are brought into contact with each other, their charges are neutralized, and they flocculate together. Thus a mixture of the hydroxides is formed. When there is an excess of one of the sols, the less abundant sol will be recharged. The hydrosols are able to migrate in ground water and surface waters under suitable conditions.

If a colloidal solution containing ferric and manganic hydroxide is brought into contact with an electrolyte, the separation of the two metals, according to Behrend (1924), starts with the coagulation of the bulk of the manganic hydroxide, while iron still remains, largely or entirely, in solution. Behrend's laboratory experiments showed that the addition of electrolytes to solutions containing an excess of

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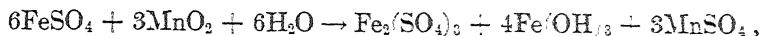
iron over manganese always caused the separation of a mixture of the hydroxides rich in manganese first, followed later by a great quantity of an iron-rich mixture of the hydroxides. Oxidate sediments rich in manganese and containing varying amounts of iron are produced by this process in Nature, such as the lake and bog iron ores (see chap. 33). Micro-organisms evidently play a part in their formation (Aschan, 1932), but the details of this process are not definitely known. The observations on some lake iron ores of Finland (Aarnio, 1917) established the fact that the separation of iron and manganese may assume a decidedly local character and that nearly pure ferric hydroxide may become deposited in certain parts of the bottom of a lake, whereas in other parts the ore is very high in manganese.

The $\text{Mn}(\text{OH})_4$ and MnO_2 sols and gels, being negatively charged, readily adsorb cations present in solution, as has been shown by laboratory experiments. Owing to its acid character, manganic hydroxide may also form adsorption compounds, such as BaMn_2O_5 , $\text{Mn}^{2+}\text{Mn}_4^{2+}\text{O}_5$, and others. Consequently, the oxidate sediments rich in manganese often contain notable amounts of the following elements: Li, K, Ca, Ba, B, Ti, Co, Ni, Cu, Zn, Tl, Pb, W, and many others. Manganese-rich bog ores may contain as much as 2.4 per cent Zn; 4.88 per cent WO_3 is reported in psilomelane and 8 per cent Zn in cryptomelane. Wad may contain 2.82 per cent NiO, 8.33 per cent CoO, 9.53 per cent BaO, and up to 14 per cent CuO.

Unlike ferric hydroxide, which is able to retain a part of its hydroxyl groups, manganic hydroxide is soon decomposed into the peroxide, MnO_2 , and water. The peroxide is the most common and most abundant of the compounds of manganese found in Nature. Pyrolusite contains 1–2 per cent H_2O , psilomelane 4–6 per cent, and wad up to 21 per cent. Most of the water in wad is adsorbed. The metastable $\text{Mn}(\text{OH})_3$ so far has not been reported to occur as a mineral. It may also be oxidized to $\text{Mn}(\text{OH})_4$ or become converted into manganite, MnOOH , by a partial dehydration; this mineral corresponds to goethite, $\alpha\text{-FeOOH}$, in composition. Complete dehydration leads to braunite, which corresponds to hematite. Manganous hydroxide, $\text{Mn}(\text{OH})_2$, like ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is unstable and is converted into $\text{Mn}(\text{OH})_3$, perhaps still more rapidly than $\text{Fe}(\text{OH})_2$ into $\text{Fe}(\text{OH})_3$.

There is still another possibility of the separation of iron and manganese on the Earth's surface, viz., by the action of solutions containing ferrous or ferric sulfate, derived from the weathering of iron

sulfides, on iron- and manganese-bearing carbonates or oxidate sediments. The process, represented by the equation



causes the extraction and migration of manganese, with a corresponding enrichment of iron. Manganese, when reprecipitated, may form deposits of considerable purity. In the presence of limestone, ferrous and ferric sulfate react therewith and produce carbon dioxide, ferric hydroxide, and calcium sulfate. The reaction between manganous sulfate and limestone requires the presence of atmospheric oxygen and results in the separation of hydroxides and oxides of manganese. These processes may also lead to the separation of iron and manganese, but often only iron and manganese hydroxide sols of a relatively high stability are produced at the initial stages.

Unlike iron monosulfide, manganese sulfide goes promptly into solution, as bicarbonate, under the action of carbon dioxide-bearing waters which contain humic substances. MnO_2 precipitated during the oxidation of such solutions may be reconverted into sulfide; and thus the cycle may go on, finally leading to the migration of manganese and its separation from iron.

The sedimentary minerals of manganese are oxides, hydroxides, and carbonates. Manganite, pyrolusite, manganomelane, and rhodochrosite are common in sedimentary deposits of manganese, but braunite and hausmannite are rare. It should be noticed that along with Mn^{4+} there also occurs Mn^{3+} , probably derived from Mn^{2+} compounds originally present:



(Behrend, 1924). Tripositive manganese occurs in manganite, braunite, and hausmannite in the weathering zone. Manganite is readily oxidized to the stable pyrolusite by atmospheric oxygen. Some manganous compounds, e.g., szmikite, $\text{Mn}[\text{SO}_4] \cdot \text{H}_2\text{O}$; mallardite, $\text{Mn}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$; and rhodochrosite, MnCO_3 , are also found in the oxidation zone. As a rule, they are more stable than the corresponding ferrous compounds.

The content of manganese in sediments and their derivatives is illustrated by the analyses presented in Table 31.4. A comparison of the manganese content in the different iron ores of marine origin shows that manganese tends to become concentrated in the siderite

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ores. The content of manganese in the red clay is considerably in excess of the average content in igneous rocks.

MANGANESE IN METAMORPHIC ROCKS

Unlike ferric hydroxide and oxide, which in metamorphic processes are readily converted into magnetite, Fe_3O_4 , the manganese oxides and hydroxides only exceptionally form hausmannite, Mn_3O_4 . Silicate minerals of manganese often result from the metamorphic changes, the reason being that the higher oxides of manganese have

TABLE 31.4
CONTENT OF MANGANESE IN SEDIMENTS AND THEIR DERIVATIVES

Material	Mn (g/ton)
Sandstones, composite (H. N. Stokes in Clarke, 1924)	trace
Shales, composite (H. N. Stokes in Clarke, 1924) . . .	trace
Limestones, composite (H. N. Stokes in Clarke, 1924)	385
Shales and phyllites, average (Hevesy, Merkel, and Würstlin, 1934)	890
Hydrolyzate sediments, average (Minami, 1935b) . .	620
Red clay, average (Hevesy, Merkel, and Würstlin, 1934)	1,770
Laterite-bauxite ores (Landergren, 1948)	800
Bog iron ores, Finland (Landergren, 1948)	74,500
Marine oolitic-siliceous iron ores (Landergren, 1948) .	1,600
Oolites, Scania, Sweden (Palmqvist, 1935; calculated by Landergren, 1948)	1,800
Marine siderite ores (Landergren, 1948)	2,600
Siderites, Scania, Sweden (Palmqvist, 1935; calcu- lated by Landergren, 1948)	2,800

relatively low heats of formation. Accordingly, they are readily decomposed. The manganous oxide, MnO , formed as a product of decomposition, is more basic than, for example, ferric oxide, Fe_2O_3 . Therefore, it reacts readily with silica to form silicates, chiefly rhodonite and, in the presence of an ample supply of alumina, spessartite. For similar reasons manganous carbonate, which is decomposed more readily than calcium carbonate, is converted into silicates in metamorphic processes.

Jakob (1933) found that manganese silicates containing Mn^{3+} are always younger than those with Mn^{2+} , because hydrogen peroxide is liberated by acid solutions from MnO_2 and the hydrogen peroxide reduces manganese to the bivalent state in acid solution. Therefore, the Mn^{3+} silicates can form only after no more hydrogen peroxide is produced.

MANGANESE IN THE BIOSPHERE

Manganese is essential to both plants and animals. It is present in all plants, and its content varies according to that of the soil. Mitchell (1944) reports a manganese content of 200 g. ton upward in the soil. Manganese is a factor in plant growth, but an excess is definitely toxic. Many aqueous plants are able to accumulate manganese as $\text{Mn}(\text{OH})_4$. Manganese has a role in the reduction of nitrates, both in green plants and in green algae. It is enriched in coal ashes, but the degree of enrichment is rather low (Goldschmidt and Peters, 1933c).

Manganese is a microconstituent of higher animals. It is an enzyme activator and has a role in bone development, in growth, and in reproduction. Marine animals are richer in manganese than the terrestrial animals are. A mussel, *Pinna squamosa*, contains a manganese protein compound, pinnaglobulin, in its blood.

MANGANESE ORES

The decomposition of rocks rich in manganese causes the formation of hydroxides and oxides of this metal, with a resulting enrichment. This process takes place in the oxidation zone near the surface and is promoted by a warm and humid climate.

The manganese-rich oxidates form the most important ores of manganese. Their mineralogical composition is frequently rather complicated. Manganese dioxide as pyrolusite, manganomelane, and wad is the most important constituent of these deposits. Other oxides and hydroxides, e.g., braunite, manganite, and hausmannite, are less important. Rhodochrosite may also form deposits of technical importance, and manganese-bearing limonite and siderite are sometimes used as manganese ores. The importance of the manganese silicates is small.

The biggest and most important manganese deposits in the world are those in the Chiaturi district of Caucasia in Russia. They consist essentially of pyrolusite. Some deposits in Cuba resemble the Caucasian manganese ores.

RHENIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

RHENIUM, along with the short-lived radioactive elements, is remarkable for its very low cosmic abundance. It has not been detected in the solar atmosphere. Its geochemical behavior was investigated by Noddack and Noddack (1931*a*, 1934). The abundance of rhenium in meteorites and igneous rocks is presented in Table 32.1, which is based on information given by the above-mentioned scientists.

TABLE 32.1
ABUNDANCE OF RHENIUM

Material	Re (g/ton)
Meteoritic irons	0.0082
Troilites	0.001
Silicate phase of meteorites	0.0008
Chondrites	0.0023
Igneous rocks	0.001

Rhenium and manganese belong to the same subgroup of the Periodic System. Therefore, the chemical properties of rhenium resemble those of manganese in many respects. However, the manner of occurrence of rhenium in Nature differs sharply from that of manganese. The abundance figures given in Table 32.1 show that rhenium is, contrary to manganese, strongly siderophile, a result corroborated by its manner of occurrence in the upper lithosphere. Rhenium does not follow manganese at all but is found in the company of molybdenum, to which it bears a resemblance in certain of its chemical properties.

The radioactive rhenium isotope, Re^{187} , is a natural β -emitter with a half-life of $4 \cdot 10^{12}$ years. Its stable decay product is the osmium isotope, Os^{187} .

RHENIUM IN IGNEOUS ROCKS

Geochemically, the most characteristic feature of rhenium is its strongly dispersed manner of occurrence. Its very low abundance and

chemical similarity with many of its neighbors in the Periodic System are displayed by the fact that it never forms independent minerals but is always concealed, in small amounts, in the structures of other minerals. According to Noddack and Noddack (1931a), the most part of rhenium, like that of many other siderophile metals, is separated from the crystallizing magma in the early sulfide fraction, in which rhenium, owing to its pronounced affinity for sulfur, is notably concentrated. Consequently, the early-separated oxide and silicate minerals are poor in rhenium, the content being less than 0.0001 g/ton in eclogites and in other early magmatic rocks and minerals. Similarly, the rhenium content of the early-separated platinum metals is low. The only exception to this rule is chromite, which often has a content of 0.02 g/ton Re. The early magmatic sulfides of the pyrrhotite-pentlandite paragenesis contain, on an average, 0.02 g/ton Re, or approximately twenty times as much as the average rhenium content of igneous rocks. In the upper lithosphere, rhenium seems to be a sulfophile element.

Minerals separated during the main stage of crystallization have an average content of 0.001 g/ton Re (Noddack and Noddack, 1931a). A notable concentration of rhenium occurs in pegmatites and, partly, also in pneumatolytic rocks, the maximum being met in columbates, tantalates, thortveitite, zircon, and particularly gadolinite, $\text{Y}_2\text{Fe}[\text{O}|\text{BeSiO}_4]_2$. Noddack and Noddack report up to 1.1 g/ton Re in gadolinite and an average of 0.015 g/ton in a composite sample of Norwegian columbate- and tantalate-bearing pegmatites. In all these minerals rhenium is enriched well above its average content in igneous rocks. The hydrothermal rocks, on the other hand, are low in rhenium. According to Noddack and Noddack, hydrothermal sulfides formed at low temperatures are low in rhenium, whereas relatively high contents are found in some hydrothermal selenides. During the later stages of crystallization rhenium is present as the relatively stable perrhenate ion, $[\text{ReO}_4]^-$, being separated, as sulfide, only in the presence of heavy metals, although small quantities may become accommodated in the structures of columbate, tantalate, molybdate, and tungstate minerals.

The highest rhenium content found in any mineral is 0.25 per cent Re in a molybdenite from Lainejaur, Sweden (Aminoff, 1943). The high rhenium content of molybdenite has already been recorded by Noddack and Noddack (1931a). The explanation is the isomorphism of molybdenum sulfide, MoS_2 , and rhenium sulfide, ReS_2 , and the

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similarity of the ionic radii of Mo^{4+} (0.68 kX) and Re^{4+} (0.56 kX). As is well known, molybdenite is most abundant in pegmatites and pneumatolytic rocks.

CYCLE OF RHENIUM

The cycle of rhenium is known very incompletely. During weathering, rhenium goes into solution as soluble perrhenate. The residates and hydrolyzates are practically free of rhenium; the content reported by Noddack and Noddack (1931a) is less than 0.001 g/ton. Rhenium, as perrhenate, is evidently present in sea water, although the concentration must be very low. The evaporates contain less than 0.001 g/ton Re. On the other hand, rhenium seems to become notably concentrated in bituminous sediments, especially in sulfur-bearing oozes, like many other heavy metals. Goldschmidt (1937b) has found 0.01 per cent Re in the molybdenite from *Kupferschiefer* at Mansfeld in Germany; but this evidence is not conclusive because the mineralization of these shales is believed to be largely caused by the introduction of postdiagenetic hydrothermal solutions. So far, the *Kupferschiefer* has been the only known commercial source of rhenium which was recovered, as a by-product, during the metallurgical treatment of the Mansfeld ores.

Information regarding the biogeochemistry of rhenium is lacking altogether.

ABUNDANCE AND GEOCHEMICAL CHARACTER

IRON is the chief member in a series of elements consisting of titanium, vanadium, chromium, manganese, iron, cobalt, and nickel, which have the atomic numbers from 22 to 28, inclusive. Goldschmidt (1929) called this series the iron family. The name adopted by Landergren (1943) is the ferrides. As in the lanthanide series and in the transuranium elements (see chaps. 18 and 46), the incorporation of new electrons in the ferrides takes place in deeper shells, and the outer shells remain intact. This property causes the marked chemical similarity of the elements belonging to such series.

Figure 2.2 shows that iron and magnesium, among all metals, have the highest cosmic abundance. Iron is twice as abundant as magnesium in the solar atmosphere, and the same abundance ratio also prevails in the meteorites (see Table 2.3). The bulk of all meteorites consists of stones which carry considerably more magnesium than iron (see Table 1.3), but the pure irons are nearly totally devoid of magnesium. In terrestrial igneous rocks, iron again is somewhat more than twice as abundant as magnesium. However, it is decidedly less abundant than aluminum.

It is evident that iron, from a geochemical point of view, is the most important metal. Along with sulfur and oxygen, iron is the foundation of all considerations dealing with the geochemical character of other elements. The abundance values of iron are presented in Table 33.1, and they show that the content of iron in the metal phase of the meteorites is higher than in the other two phases. The absolute abundance of iron in the metal phase is higher than that of any other metal. Therefore, iron is the prototype of the siderophile elements. Iron has a high affinity for sulfur, and consequently it is pronouncedly chalcophile. Considerable amounts of iron are present in the lithosphere, which shows the lithophile character of this metal. With reference to its terrestrial manner of occurrence, iron must also

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be included in the group of the biophile elements; and in the upper lithosphere it is oxyphile.

A general comparison of the geochemical properties of the elements belonging to the ferride group shows that their lithophile tendency decreases with increasing atomic number from titanium to nickel. The last three members of the group, viz., iron, cobalt, and nickel, have the most marked siderophile and chalcophile properties.

IRON IN IGNEOUS ROCKS

The earliest products of magmatic differentiation include oxide minerals of iron, which usually are titaniferous, and sulfide segregations, which consist chiefly of the iron monosulfide, FeS. Therefore, it may be concluded that iron is the most common and the most important constituent of the early magmatic nonsilicate segregations.

TABLE 33.1
ABUNDANCE OF IRON

Material	Fe (Per Cent)
Iron meteorites (Goldschmidt, 1937 <i>b</i>) . . .	90.5
Troilites (Noddack and Noddack, 1930)	61.10
Silicate meteorites (Goldschmidt, 1937 <i>b</i>) . . .	13.04
Igneous rocks (Goldschmidt, 1937 <i>b</i>)	5.00

In the early-formed silicate rocks, viz., dunites, the content of iron is rather low, and magnesium preponderates over iron. According to the average chemical composition of the calc-alkalic igneous rocks calculated by Daly (1933; see Table 5.32), the total iron content of the various classes is given in the accompanying tabulation.

Rock	Fe (Per Cent)
Dunite	6.30
Hornblendite	11.76
Gabbro	8.84
Diorite	5.63
Granodiorite	3.28
Granite	2.48

These percentages show that the highest content of iron is met at the outset of the main stage of the crystallization, here represented by hornblendites. With proceeding differentiation, the content of iron decreases, but the decrease is not so pronounced as is that of magnesium (see chap. 5). Although both iron and magnesium are more abundant in basic rocks than in acidic rocks, the Fe:Mg ratio changes during the differentiation, and iron finally becomes enriched in regard to magnesium during the last steps of the main stage of

crystallization. This phenomenon was explained, on crystal chemical grounds, in chapter 5.

Wickman (1943) pointed out that the content of ferric iron does not change much with proceeding differentiation. On the other hand, the content of ferrous iron decreases more sharply and is mainly responsible for the increase in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. The Fe^{3+} ion may be considered so immobile that it is taken up in a suitable structure under any conditions. The Fe^{2+} ion becomes enriched in the melt with respect to Mg^{2+} ; but this phenomenon is probably somewhat obscured by the simultaneous oxidation of ferrous iron. In spite of the oxidation, the content of Mg^{2+} decreases much more rapidly than does the content of Fe^{2+} , and therefore, in an environment in which the oxidation of Fe^{2+} cannot take place, the residual liquor will be rich in iron. The ferric iron produced during the differentiation is partly incorporated in silicate structures and partly in magnetite. The content of ferrous iron is always high enough to prevent the formation of hematite.

Native iron is a rare constituent of igneous rocks, and it is found only in a few rocks, particularly in basalts, either as pure iron or alloyed with nickel, e.g., as awaruite and josephinite. The iron-bearing rock-making minerals contain bi- and trivalent iron. The radius of Fe^{2+} is 0.83 kX, and the radius of Fe^{3+} is 0.67 kX.

Owing to the difference in their ionic sizes, ferrous and ferric iron differ from each other with respect to their manner of occurrence in mineral structures; i.e., Fe^{2+} accompanies Mg^{2+} (radius 0.78 kX), which it replaces diadochically, but Fe^{3+} usually substitutes for Al^{3+} (radius 0.57 kX). The Fe^{2+} - Mg^{2+} diadochy in mineral structures is complete and continuous, whereas the Fe^{3+} - Al^{3+} diadochy is less extensive because there is considerable difference in the sizes of these ions. The Fe^{3+} - Al^{3+} diadochy seems to occur on a more substantial scale only when aluminum occurs as a cation outside the silicon-aluminum network in the aluminum silicates, and not as a constituent of a complex anion, replacing silicon within the oxygen tetrahedra of the aluminosilicates.

According to the calculations of Clarke (1924), the feldspars are quantitatively the most important silicate minerals of igneous rocks. Schiebold (1931) has shown, on thermochemical grounds, that ferrous iron cannot form a feldspar structure. The study of the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ has not revealed the presence of an artificial ternary compound. On the other hand, Schiebold pointed out that ferric iron

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may form a feldspar structure. The experimental evidence furnished by P. Hautefeuille in 1880, by Hautefeuille and A. Perrey in 1888, and by Faust (1936) shows that ferric compounds corresponding to leucite and potash feldspar actually form in the ternary system $K_2O-Fe_2O_3-SiO_2$. The iron content of the feldspars is low, with the exception of a ferri ferrous orthoclase from Madagascar, reported to contain 2.88 per cent Fe_2O_3 ; and therefore it is evident that the ferric feldspars and feldspathoids are not stable under the circumstances usually present in igneous rocks. It is possible that the hematite flakes which are often present in the feldspars and which cause the red color of aventurine and other feldspars were formed by the decomposition and exsolution of the ferric feldspars, which are at least partially isomorphous with the alkali feldspars and the plagioclases.

It is evident that the bulk of iron in the igneous rocks is found in the dark constituents. The most important iron-bearing minerals of igneous rocks include the pyroxenes, the amphiboles, and the ferromagnesian micas. Only the iron orthosilicate is known to crystallize in the system $FeO-SiO_2$; it is fayalite, $Fe_2[SiO_4]$, the iron end-member in the olivine group. The metasilicate of iron, which is the iron end-member of the series of the orthorhombic pyroxenes, does not crystallize from artificial silicate melts. This fact explains the petrographic observation that enstatite, which is the magnesium end-member of the series of the orthorhombic pyroxenes, occurs in Nature as a rather pure compound, whereas the pure iron end-member, hypersthene, is unknown. The monoclinic pyroxene clinoferrosillite, $Fe_2[Si_2O_6]$, is met in Nature, but evidently it crystallized at a low temperature, and it is only a mineralogical curiosity. No binary compound is known in the system $Fe_2O_3-SiO_2$.

Along with the iron-bearing silicate minerals, sulfide and oxide minerals of iron are present in igneous rocks. According to Noddack and Noddack (1931a), the iron content of the primary magmatic sulfides, on an average, is 53.9 per cent. The sulfide and oxide minerals of iron are accessory constituents of igneous rocks. The most important species are the following:

Magnetite,	Fe_3O_4	(72.4 per cent Fe)
Ilmenite,	$FeTiO_3$	(36.8 per cent Fe)
Pyrrhotite,	FeS	(60.4 per cent Fe)
Pyrite,	FeS_2	(46.6 per cent Fe)

According to Newhouse (1936), magnetite is more abundant than ilmenite in salic and extrusive rocks, whereas ilmenite predominates

over magnetite in femic rocks. The exsolution intergrowths magnetite-ilmenite are found in nearly all igneous rocks. There are several other exsolution intergrowths: the ilmenite-hematite intergrowths are rather common in granites, norites, and anorthosites; magnetite-ilmenite-spinel intergrowths occur chiefly in gabbros and norites.

Newhouse's calculations showed that pyrrhotite and chalcopyrite are the most common accessory opaque minerals of igneous rocks. According to Ramdohr (1940), magnetite is much more abundant than all the other opaque constituents. It forms, on an average, about half the total quantity of the accessory opaque minerals. Ilmenite comes next, being followed by pyrrhotite; but the other sulfides are less abundant.

Ramdohr (1940) also found hematite, $\alpha\text{-Fe}_2\text{O}_3$, as a constituent of igneous rocks, but it is uncommon, and its quantity is considerably lower than the quantity of magnetite and ilmenite. Ramdohr thinks that hematite found in igneous rocks usually is not a primary result of crystallization but rather has formed by various alteration processes.

During the crystallization of alkalic magmas, which belong to the agpaite type, iron, contrary to its behavior in the calc-alkalic rocks, tends to remain in the residual melt. It becomes notably enriched during the pegmatitic stage of crystallization and gives rise to nepheline syenite pegmatites, which consist mainly of dark iron-bearing minerals, such as the alkali amphiboles and pyroxenes.

Along with the pyroxenes, amphiboles, and ferromagnesium micas, the igneous rocks contain a number of other iron-bearing minerals which, however, usually do not possess much geochemical importance. Numerous iron minerals belong to the spinel group, viz., hercynite, FeAl_2O_4 ; magnesioferrite, MgFe_2O_4 ; franklinite, ZnFe_2O_4 ; jacobsonite, MnFe_2O_4 ; and trevorite, NiFe_2O_4 . Also magnetite and chromite are members of the spinel group. Other oxide minerals of iron include columbite and tantalite (see chap. 26). Molysite, FeCl_3 , and some other complex iron chlorides are rare constituents of volcanic incrustations, but lawrencite, FeCl_2 , is found only in meteorites. A number of sulfides and sulfosalts of iron occur in sulfide-ore bodies and in mineral veins. Siderite, FeCO_3 (48.2 per cent Fe) is present in hydrothermal veins. The phosphate minerals of iron include, among others, triphylite, lithiophilite, and triplite (see chap. 31); vivianite, $\text{Fe}_3^{2+}[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$, which is found in hydrothermal veins and also as a secondary mineral in bog iron ores and fossil cavi-

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ties; and strengite, $\text{Fe}^{3+}[\text{PO}_4] \cdot 2\text{H}_2\text{O}$. Like the phosphates, the arsenates are numerous. Symplectite, $\text{Fe}_3^{2+}[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$, corresponds to vivianite in composition. A number of iron-bearing borate minerals are known in pegmatites. The wolframates ferberite and wolframite were discussed in chapter 29.

IRON IN THE BIOSPHERE

Iron is a constituent of all living tissues, both vegetable and animal. In green plants iron is a constituent of the chloroplasts and is necessary for the formation of the chlorophyll. It affects the growth of the plants. Iron is often somewhat enriched in coal ashes.

In the soil, ferric iron may oxidize organic matter and consequently becomes reduced to the ferrous state. Ferrous iron, in turn, may be reoxidized, and thus iron acts as a continuous oxidizing agent, which is partly responsible for the oxidation of carbon compounds into carbon dioxide. Consequently, iron plays the role of a catalyst in the cycle of carbon.

A porphyrin derivative of iron is found in animal tissues. The blood of many animals contains an iron-bearing respiratory pigment: the green chlorocruorin occurs in the blood of some marine worms, the red hemoerythrin in some lower animals, the red erythrocrurorin in many invertebrates, and the red hemoglobin in higher animals. Some enzymes are iron-bearing protein complexes.

The foremost biological function of iron is its action in transporting oxygen in organisms during respiration from the environment to the oxidizable compounds of tissues. Hemoglobin is a chromoprotein which contains a complex iron derivative of a porphyrin. Hemoglobin is able to combine readily with oxygen to oxyhemoglobin without the oxidation of iron. Oxyhemoglobin dissociates just as readily into oxygen and hemoglobin and is responsible for the transport of oxygen in the blood. Iron acts as a catalyst in all cellular respiration.

Some bacteria living in iron-bearing waters are characterized by a cell membrane impregnated with ferric hydroxide, which accumulates from water. According to previous belief, the energy needed by the life-processes of these bacteria was obtained from the oxidation of ferrous iron to ferric iron. However, it is now known that the metabolism of these bacteria does not differ from the metabolism of other micro-organisms.

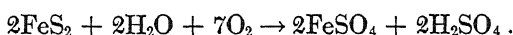
Humboldtine, $\text{Fe}[\text{C}_2\text{O}_4] \cdot 2\text{H}_2\text{O}$, is a natural hydrous ferrous oxalate.

CYCLE OF IRON

The cycle of iron and the cycle of the ferrides, in general, form one of the most important branches of geochemistry, both scientifically and technically. The most important step in the cycle of iron is the oxidation of ferrous to ferric iron by atmospheric or dissolved oxygen. The oxidation is the ultimate cause of the precipitation of iron and may lead to the formation of extensive iron deposits. The ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is still rather strongly basic, whereas the basic properties of ferric hydroxide, $\text{Fe}(\text{OH})_3$, are so weak that ferric salts are hydrolyzed in natural waters under the formation of ferric hydroxide. The primary factors affecting the manner of migration of iron are the presence or absence of oxygen and carbon dioxide.

Both ferrous and ferric iron are present in igneous rocks. When oxygen is absent, ferrous iron is relatively readily dissolved in water containing carbon dioxide. Ferrous bicarbonate, $\text{Fe}(\text{HCO}_3)_2$, is thereby formed, and it is partly dissociated in aqueous solutions. Ferrous carbonate, FeCO_3 , is precipitated when carbon dioxide is removed from solution, e.g., when the partial pressure of carbon dioxide diminishes with diminishing atmospheric pressure; when carbon dioxide escapes because of an increase in temperature; or when it is utilized by plants in photosynthesis. Precipitated ferrous carbonate is often found in bogs.

When the sulfide minerals of iron are oxidized, ferrous sulfate and sulfuric acid are the first products to be formed:



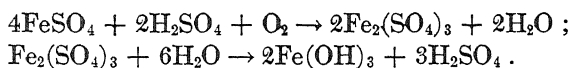
Sometimes ferrous chloride, FeCl_2 , may be present in the weathering solutions. However, compared with the content of ferrous bicarbonate in solution, the content of ferrous sulfate is small, and the content of ferrous chloride negligible.

Surface waters are poor in ferrous bicarbonate, but in spring waters containing much carbon dioxide this compound may be rather abundant.

Both ferrous carbonate and ferrous sulfate are unstable in the presence of atmospheric and dissolved oxygen and are likely to become converted into ferric compounds as soon as possible. Ferrous bicarbonate is decomposed into ferric hydroxide and carbon dioxide, probably with the partial action of bacteria. Ferric iron does not form a bicarbonate. Alkali carbonates in solution may precipitate ferrous

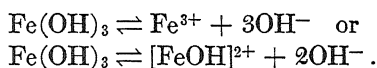
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carbonate when brought into contact with dissolved ferrous sulfate. Ferrous sulfate and sulfuric acid react under the presence of oxygen to produce ferric sulfate, which is quickly hydrolyzed to ferric hydroxide:



Micro-organisms may participate in the formation of sulfuric acid.

Ferric hydroxide is partly dissociated, as follows:



The $[\text{FeOH}]^{2+}$ ions are more important than the Fe^{3+} ions. The solution may contain Fe^{3+} ions in notable amounts only if the pH is less than 3. However, ferric hydroxide readily forms colloidal solutions. Thus iron is transported into the sea either as $\text{Fe}(\text{OH})_3$ sol in the presence of oxygen or as Fe^{2+} ions in the absence of oxygen and in the simultaneous presence of carbon dioxide. The transportation as Fe^{2+} ions is quantitatively more important than the transportation as colloidal ferric hydroxide, but less important than as organic colloids or adsorbed thereon.

Contrary to the alkali and the alkaline-earth metals, iron is not stable in weathering solutions. The comparison with manganese shows that the iron compounds formed during weathering are less readily soluble and less stable than the corresponding compounds of manganese.

Magnetite and ilmenite are rather stable against weathering. They are largely collected in the resistates and may form local concentrations of iron therein. However, the oxide minerals of iron are partly converted into ferric hydroxide by the action of carbon dioxide and water. Ferrous carbonate is thereby formed as an intermediary product.

In lateritic weathering under tropical and subtropical conditions, iron is collected as ferric hydroxide in the weathering residue, along with aluminum hydroxide.

Ferric iron may be brought into solution after reduction to the ferrous state. Hydrogen sulfide produced during the decay of sulfur-bearing organic compounds is one of the most important reducing agents met in Nature and is often present in small amounts in weathering solutions. In addition, organic solutions containing humic com-

pounds also reduce ferric iron to soluble ferrous compounds. Humic complexes of iron, moreover, form colloidal solutions which are rather stable, and consequently iron is able to migrate in such a form. The content of iron in bog waters is higher than in other surface waters because stable humic complexes of iron are present therein.

Iron in the presence of oxygen may occur as ferric ions only in acid solutions. Such solutions, with a pH less than 3, are rather uncommon in Nature. In all other cases, Fe^{3+} is precipitated as ferric hydroxide, first as a colloid. Atkins (1930) remarked that the precipitation of ferric hydroxide starts at $\text{pH} = 3$, whereas the precipitation of ferrous hydroxide starts at $\text{pH} = 5.1$. However, ferrous hydroxide is unstable and unknown as a mineral; it occurs only as a mixture with ferric hydroxide. Because the precipitation of ferrous hydroxide is still incomplete at $\text{pH} = 7$, ferrous salts can be transported in considerable quantities in natural waters, but ferric salts cannot. In lake and river waters the pH is 6.5–7.0 except in calcareous regions, in which it is 8.0–8.4. In sea water, the pH usually varies from 8.1 to 8.4. Therefore, ferrous iron is no longer stable in solution in water from calcareous regions and in sea water.

Ferric iron, being able to migrate in true solution only in acid waters, differs from aluminum, which may migrate both in acid and in basic solutions, being precipitated only in the neighborhood of the neutral point (see chap. 17). When an acid weathering solution is neutralized, ferric hydroxide is first precipitated, but aluminum remains in solution until a higher pH is reached. Consequently, iron and aluminum may become separated, even though the separation is not quantitative.

Table 6.17 shows that the content of iron in sea water varies from 0.002 to 0.02 g/ton. This is an exceedingly small value and shows that sea water is by far the most iron-poor substance found in Nature. The content of iron in the purest quartz sands is about 50 g/ton, or 2,500–25,000 times as high as the iron content in the sea. Table 6.19 shows that the transfer percentage of iron is 0.00007, and therefore it is evident that a very considerable decrease of the iron content takes place in the sea, notwithstanding the large amounts added to the sea in weathering solutions. Only a small part of iron liberated during the weathering ever reaches the open ocean. The bulk is deposited in lake and bog iron ores, in oolitic iron ores, and in some iron-bearing silicates, such as glauconite and greenalite.

Oxygen is always present in the upper layers of the sea. Therefore,

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iron carried by the rivers is converted into colloidal ferric hydroxide upon reaching the sea. However, ferric hydroxide has usually already been formed in river water. Therefore, a part of the iron in the sea is present as colloidal ferric hydroxide. More, perhaps the bulk, of iron is found in particulate form. According to Harvey (1937), it is also possible that iron forms colloidal and larger aggregates of ferric phosphate with the phosphates in solution in sea water. The content of ferric hydroxide in true solution in the sea is negligible, but sea water may contain ferric hydroxide sols which behave like real ions in the extremely low concentrations that are present. In addition, there might be ferric fluoride in solution, because the fluorine content of sea water is high enough to allow the formation of this compound and perhaps of other complex fluorides also. Ferric fluoride may be used by marine plants as a source of iron. Traces of iron may also be found in sea water in the form of organometallic compounds. However, such complexes are unstable and are slowly hydrolyzed in sea water.

The biological cycle of iron in the sea forms a part of its general cycle, presented in Figure 33.1, mainly according to Cooper (1935) and Landergren (1948). The iron content of the phytoplankton organisms is relatively high and may be as much as 16 per cent of the total content of iron in sea water (Cooper, 1935). The phytoplankton organisms are able to utilize ferric hydroxide, and possibly also ferric phosphate and ferric fluoride, and to adsorb the insoluble ferric compounds as colloidal particles on their surface. Stable organic compounds of iron, on the other hand, probably cannot be utilized by plants. The plants are eaten by animals, and much of the iron returns to the sea in the excrement and upon the death of the animals. Thus iron again becomes available, in a reasonably short period of time, for the diatoms for another growth cycle. In spite of its low content in sea water, iron consequently supports the diatom population. As pointed out by Cooper (1935), marine diatoms must be very well adapted to use the traces of iron which are available in the sea.

In an acid solution under reducing conditions, iron tends to go into solution. Alkaline solutions and oxidizing conditions are most favorable for the precipitation of iron as ferric hydroxide. Like manganese, iron is preferably precipitated in oxidizing surroundings in the presence of calcareous material.

Ferrous iron preponderates over ferric iron in all classes of igneous rocks (see Table 5.32) because the amount of oxygen available in the

upper lithosphere does not suffice to oxidize the total of the electro-positive elements to their highest state of oxidation. In sediments and sedimentary rocks, on the other hand, ferric iron preponderates. With few exceptions the sediments are deposited in oxidizing sur-

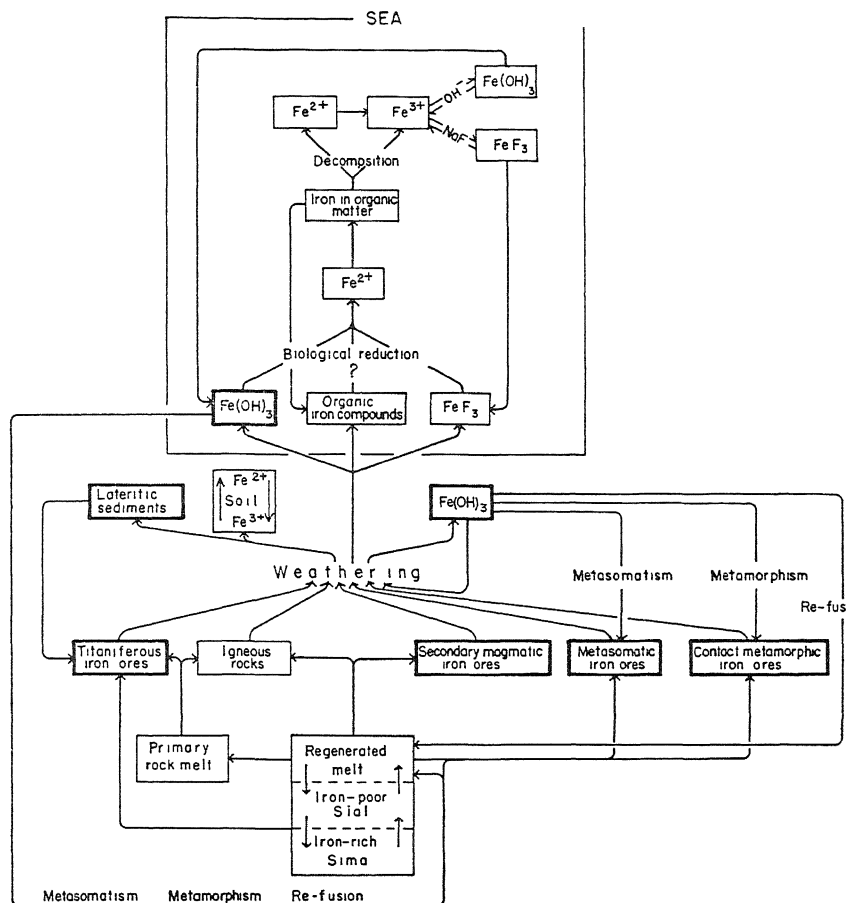


FIG. 33.1.—The cycle of iron

roundings, and this fact explains the relatively high content of ferric iron in these sediments.

The average iron content of igneous rocks calculated from Goldschmidt (1937b) and of the three main groups of sedimentary rocks calculated from Clarke (1924) is given in the accompanying tabulation. These values show that comparatively little iron is present in the residates. The reason is that the ferric constituents of rocks

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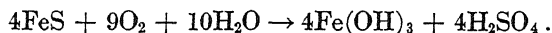
which contain the bulk of iron present in igneous rocks usually decompose during the weathering, and only such accessory constituents as ilmenite and magnetite remain unchanged. The iron content of the carbonate sediments is, at least partly, caused by impurities present in geochemically irrelevant surroundings. The hydrolyzate sediments are nearly as high in iron as are the igneous rocks, on an average. The iron content of the evaporates is very low, and iron-bearing salt minerals, such as rinneite, $K_3Na[FeCl_6]$, and douglasite, $K_2[FeCl_4] \cdot 2H_2O$, are rare. The strongest concentration of iron takes place in the oxidates in which iron (and manganese) occur as the main constituent.

Rock	Fe ₂ O ₃ (Per Cent)
Igneous rocks.....	7.15
Sandstones.....	1.41
Shales.....	6.73
Limestones.....	0.54

The precipitation of iron in the oxidate sediments takes place in a manner analogous to the precipitation of manganese (see chap. 31). With reference to marine oxidates, red clay contains somewhat more iron than do the igneous rocks, on an average, but the difference is less pronounced than with manganese.

The high iron content of the hydrolyzates is partly due to the precipitation of ferric hydroxide. In addition, the ferric hydroxide sol is positively charged and consequently flocculates with negatively charged colloids, e.g., silica and humic complexes. Nontronite, $Fe_2^{3+}[(OH)_2[Si_4O_{10}] \cdot nH_2O]$, and other iron-bearing clay minerals may ultimately result in the reaction between colloidal silica and colloidal ferric hydroxide. Nontronite is a common constituent of various clays.

Iron is also precipitated as sulfide in stagnant water in the presence of hydrogen sulfide and therefore may become incorporated in the hydrolyzates. The processes which produce hydrogen sulfide are bacterial decomposition of sulfoproteins, bacterial reduction of sulfates, and bacterial action on free sulfur. In addition, sulfides may react with carbon dioxide and water to produce hydrogen sulfide. Both dissolved iron compounds, e.g., ferrous sulfate, and colloidal and precipitated ferric hydroxide react with hydrogen sulfide, and iron sulfide is thereby produced. This shows that the cycle of iron is linked with the cycle of sulfur (see Fig. 43.1). Both FeS and FeS_2 are produced in the sulfuretum. However, the iron sulfides may also be oxidized:



The oxidation proceeds unaided by micro-organisms under aerobic conditions.

According to Newhouse (1927), marcasite is the principal form of iron sulfide arranged along stratigraphic planes in coal beds, whereas pyrite is the common form in other sediments.

Ferric hydroxide and ferrous carbonate are the most common and most important forms of reprecipitated iron in the exogenic cycle. Iron is also precipitated as sulfide; as hydrous, ferrous, and ferric silicates; and as phosphate, e.g., anapaite, $\text{Ca}_2\text{Fe}^{2+}[\text{PO}_4]_2 \cdot 4\text{H}_2\text{O}$. Other minerals formed in the zone of weathering include arsenates, e.g., scorodite, $\text{Fe}^{3+}[\text{AsO}_4] \cdot 2\text{H}_2\text{O}$, which is an alteration product of arsenic minerals, especially arsenopyrite; vanadates; tungstates; and sulfates, such as copiapite, $\text{MgFe}_4^{3+}[\text{OH} | (\text{SO}_4)_3]_2 \cdot 18\text{H}_2\text{O}$, the most common ferric sulfate; melanterite, $\text{Fe}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$, an alteration product of pyrite and marcasite; and jarosite, $\text{KFe}_3^{3+}[(\text{OH})_6 | (\text{SO}_4)_2]$, a secondary mineral of solfataric origin. Magnetite may occur as a rare oxidation product of ferrous sulfate in the zone of oxidation. Hematite is common as a weathering product of iron-bearing minerals, e.g., magnetite, siderite, and natural hydrous iron oxides.

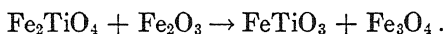
IRON ORES OF MAGMATIC ORIGIN

Iron is separated in the early crystallates during the differentiation in the form of sulfide and oxide minerals. The iron oxides may form ore bodies of high technical importance, whereas the early-separated sulfide bodies, which belong to the pyrrhotite-pentlandite paragenesis, are not classified as iron ores. On the other hand, the sulfides are important technical sources of nickel and copper and sometimes of the platinum metals. The presence of pyrrhotite is not always proof of a high temperature of crystallization, even though in the system Fe-S the monosulfide, FeS, is more stable at elevated temperatures and the bisulfide, FeS_2 , more stable at lower temperatures. Pyrrhotite is also formed when sulfur is strongly deficient, e.g., in mineral veins rich in arsenic.

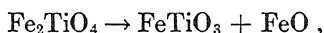
The geochemically most important magmatic oxide ores of iron are the titaniferous iron ores, the chromite ores, and the magnetite ores rich in phosphorus. According to Landergrén (1943), the average iron content of the titaniferous iron ores is 35.7 per cent Fe, and the average content of magnetite ores found in gabbros is 55.9 per cent Fe. The average content in the Grängesberg apatite-bearing iron ore in Sweden is 59.0 per cent Fe.

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Magnetite and ilmenite are the chief constituents of the titaniferous iron ores. The two minerals are sometimes found as independent grains, but usually there occur intimate admixtures consisting of ilmenite laminae of varying thickness in magnetite grains. The magnetite of igneous rocks is nearly always titaniferous (titanian magnetite), and in such magnetites Ti^{4+} evidently diadochically replaces Fe^{3+} , and, perhaps, partly Fe^{2+} . However, the titanium-iron diadochy in the magnetite structure is not very extensive at low temperatures. If the decrease in temperature during crystallization is comparatively slow, ilmenite separates from magnetite in the form of oriented inclusions. According to Foslie (1928), the miscibility of ilmenite and magnetite is very low at all temperatures. On the other hand, the iron orthotitanate, Fe_2TiO_4 , is isomorphic with magnetite and may form an extensive series of mix-crystals with it (the titanian magnetites). If there is an excess of Fe_2O_3 with respect to TiO_2 and FeO , the orthotitanate cannot be stable:



Therefore, a titanium-poor magnetite is formed. At any rate, the iron orthotitanate is stable only at elevated temperatures. At lower temperatures it is decomposed:



and the ferrous oxide is incorporated in silicate minerals.

Chromite, FeCr_2O_4 , is the main constituent of the chromiferous iron ores. Magnetite usually is nearly absent in the chromite ores. It is generally held that both titaniferous iron ores and chromite ores are magmatic segregations formed in an early stage of differentiation.

The iron ores rich in phosphorus probably were formed during a comparatively late stage in the course of magmatic differentiation. They are usually rather pure magnetite ores which do not contain appreciable amounts of titanium and chromium. They run high in phosphorus and carry notable amounts of apatite (usually fluorapatite), fluorite, and other minerals. Although the ore-forming materials were separated from the silicate melt in a rather early stage, they remained molten until the rocks of the main stage of crystallization solidified. The ore material subsequently intruded the solidified rocks as a fluid mass. Therefore, the iron ores rich in phosphorus actually belong to the pneumatolytic formations. According to Lander-

gren (1943, 1948), these ores are not primary magmatic rocks at all but are formed during the remelting of iron-rich sediments and sedimentary iron ores. The regenerated melt was intruded as an ore magma rich in iron and phosphorus. Therefore, these ores are of a secondary magmatic origin. However, the possibility must also be considered that the original material of the apatite-bearing iron ores has been leached out from rocks by hydrothermal solutions, which thereby have become enriched in iron and phosphorus and which later were subjected to paligenetic processes.

Landergren (1943) emphasized the fact that the enrichment of iron in the upper lithosphere is anomalous because it takes place in geochemically irrelevant surroundings. Actually, the terrestrial enrichment of iron should work toward the nickel-iron core.

The formation of oxide ores of iron is a question not only of the enrichment of iron but also of the enrichment of oxygen to make the formation of the ore minerals possible (Landergren, 1948). Although oxygen, in general, is of atmospheric origin, a source of oxygen might be the volatile constituents: water and carbon dioxide, which react with ferrous iron during contact metamorphism, whereby magnetite is formed. Magmatic differentiation as a mechanism producing oxide ores of iron is regulated by the physical properties and chemical composition of the primary magma and by the material of exogenic origin which is incorporated.

Landergren (1948) showed that the rule of Oddo and Harkins is not valid for the mass numbers 46–62 of the ferrides in igneous rocks and in iron ores, probably because the primary enrichment of iron takes place during the exogenic cycle. The secondary enrichment of iron takes place during the geological processes which give the products of the exogenic enrichment the properties of an iron ore. The endogenic enrichment of iron may be considerable, e.g., from 48 to 72 per cent Fe when siderite is converted into magnetite. The remobilization of iron during the endogenic cycle may take place under certain conditions, which depend on the composition of the iron-bearing material, the presence or absence of volatile constituents, and temperature. The following processes are connected in the transformation of the iron-rich sediments and sedimentary rocks: contact metamorphism, metasomatism, and the formation of a secondary mineral facies by paligenesis. The formation of the titaniferous iron ores is connected with the crystallization of basic igneous rocks, but the relationship between the silicate and the oxide fractions may be

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primary or secondary. Landergren suggested that the prerequisite for the formation of iron ores in general is the exogenic enrichment of iron. The exogenic cycle involves removal of oxygen from the atmosphere, particularly by the oxidation of iron. When sediments and sedimentary rocks are metamorphosed and are subjected to thoroughgoing changes in anatexis, a part of the oxygen bound in ferric oxide and hydroxide is released and is available for the oxidation of other substances. Therefore, iron acts as a "respiratory pigment" in the upper lithosphere (see chap. 27).

The magmatic iron ores in the wide sense of the term also include the contact metamorphic and metasomatic ores, which are formed particularly in the contact zones between silicate and carbonate rocks. Silicate magmas and their emanations react with the carbonate, giving rise to ore bodies consisting of magnetite and called skarn ores.

IRON ORES OF SEDIMENTARY ORIGIN

The iron-rich oxidate sediments which consist chiefly of ferric hydroxide and also of ferric oxide are the most important iron ores of sedimentary origin. They are usually manganiferous (see chap. 31). The iron-rich oxidates are deposited either in fresh water or in the shallow parts of the sea. The deposition in the sea is more important than the deposition in fresh water, in both geochemical and technical respects, when the extent of the deposits formed is considered. The marine oxidates are deposited from weathering solutions of continental origin, and they are precipitated largely as gels. Ferric hydroxide may be formed only locally by the action of FeCl_3 and FeF_3 vapors on sea water in submarine volcanic processes. The texture and chemical composition of marine oxidates varies very much. Often the ferric hydroxide has been precipitated in the form of concretions or rounded nodules with concentric structure, called oolites; the matrix between the oolites consists of earthy ferric hydroxide. Such is the texture of the oolitic iron ores. According to Correns (1943), the iron-rich marine sediments, e.g., the Jurassic oolitic Minette ores of Alsace-Lorraine in France and the Silurian Clinton-type deposits of the Appalachians in the United States, were originally deposited in oxygen-bearing sea water, in which the transportation of colloidal ferric hydroxide was so much in excess of other substances that sediments with 30–50 per cent Fe were deposited. However, a part of these ores may originally have been precipitated as ferrous carbonate from bi-

carbonate solutions in the absence of oxygen or as ferric hydroxide in the presence of oxygen.

According to Correns and von Engelhardt (1941), goethite (*Nadeleitenerz*), $\alpha\text{-Fe}^{3+}\text{OOH}$, is the most common mineral of the oolitic iron ores. Lepidocrocite (*Rubinglimmer*), $\gamma\text{-Fe}^{3+}\text{OOH}$, is rare, as is hematite. Magnetite and maghemite, $\gamma\text{-Fe}_2\text{O}_3$, are also present in the ores; and there occur quartz, siderite and other carbonates, and iron silicates, such as cronstedtite, $\text{Fe}_4^{2+}\text{Fe}_2^{3+}[(\text{OH})_8|\text{Fe}_2^{3+}\text{Si}_2\text{O}_{10}]$, and members of the mica and chlorite groups. The generic name limonite is often used for mixtures of goethite and lepidocrocite. Although these two minerals are identical chemically and both crystallize in the orthorhombic system, their crystal structures are different. The silica present in the iron silicates of the oolitic iron ores was originally precipitated as a gel. The silica sol is negatively charged and therefore may partly flocculate with the positively charged ferric hydroxide sol. Many elements are also found in the marine iron ores which were originally incorporated by adsorption, e.g., vanadium, phosphorus, arsenic, antimony, and selenium.

Correns (1941, 1942, 1947) remarked that the content of iron in sea water depends on the content of oxygen and on the pH. The content of oxygen is high enough to oxidize all iron to the ferric state, and, because the pH always is higher than 6, iron is precipitated as ferric hydroxide. Therefore, the content of iron in the sea is kept negligible, and no sediments rich in iron may be expected to be deposited from such an iron-poor solution. The sea water during the earlier geological periods was also low in iron, as is shown by the low content of iron in the oceanic salt deposits: a content of only 0.04 per cent Fe_2O_3 in red carnallite causes a remarkably deep color.

The material which is mechanically transported to the sea is low in iron. The iron content of river water is less than 1 mg/l. Consequently, it must be assumed that the marine iron ores are a result of weathering under very specific and temporary conditions which no longer exist. The amount of iron supplied to the sea during their formation must have been very large.

The lake and bog iron ores contain ferric hydroxide (limonite), iron silicates, iron carbonate, and iron sulfide, along with various impurities. Their phosphorus content usually is high, and they contain manganese in varying amounts (see chap. 31). A number of theories on the precipitation of iron in these sediments and in ortstein formations has been presented. The ferrous bicarbonate found in the carbon di-

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oxide-bearing waters may be decomposed when carbon dioxide is removed, whereupon ferrous carbonate is precipitated and subsequently converted into ferric hydroxide. Micro-organisms are believed to play a role in this process. It is known, in addition, that ferrous salts have already been oxidized to ferric salts in the lakes prior to their migration to salt water. The humic substances present in water form iron complexes which are rather stable and consequently may be transported long distances. When these complexes are brought into contact with atmospheric or dissolved oxygen, they are oxidized to carbon dioxide and ferric hydroxide. In neutral and alkaline solution the oxidation takes place almost immediately, but in acidic solution it is slower. Gruner's (1922) studies revealed that the precipitation of iron from organic solutions exposed to air is usually slow and may be stopped altogether. In the presence of carbonates of the alkali metals or of the alkaline-earth metals, iron is precipitated as hydroxide, but the precipitation is incomplete. Iron is never completely removed from the natural organic solution, and 2–8 g/ton Fe remain in river water. On the other hand, all iron but approximately 1 g/ton is precipitated from surface waters free of organic matter.

Bacteria promote the precipitation of iron as ferric hydroxide from lake and sea water. According to Aschan (1932), the humic iron complexes are decomposed by micro-organisms, and thereby ferric hydroxide is precipitated.

The iron sulfides of sedimentary origin are pyrite and marcasite, FeS_2 ; melnikovite, probably amorphous FeS_2 ; and hydrotroilite, $\text{FeS} \cdot n\text{H}_2\text{O}$. Pyrite and marcasite are common in sandstones, shales, limestones, and coal. Iron sulfide may be precipitated from solutions containing humic complexes of iron in the absence of oxygen. Sometimes the content of iron sulfide in hydrolyzate sediments is high enough to give rise to pyrite deposits in shales and in schists which are their metamorphic derivatives. Such deposits are characterized by the presence of certain elements which distinguish them from the hydrothermal pyrite deposits. Carstens (1941*a, b*, 1943) found that the Norwegian pyrite ores of sedimentary origin contain more carbon, arsenic, manganese, and phosphorus but less silver, copper, zinc, and selenium than do the pyrite ores of hydrothermal origin. In addition, the sedimentary pyrites are characterized by the predominance of nickel over cobalt, whereas the reverse is the case in the pyrites of the hydrothermal veins.

Oxide sediments of iron are also believed to be formed as hot-spring deposits on volcanic areas or as a result of submarine volcanic activity. Such sediments are of widespread occurrence in the geological column. They are found, e.g., in the Lake Superior region in North America and in the Brazilian Shield. They differ from the oxides normally deposited in lake and sea water, in that they usually do not carry considerable amounts of adsorbed substances but consist of rather pure ferric hydroxide or of hematite and magnetite formed during the metamorphism of the hydroxide.

The oxides connected with volcanic activity are usually attributed to submarine eruptions of basic lavas and copious amounts of hydrothermal solutions produced in a closed basin. The hot-spring theory is often rejected on the grounds that the springs would need to have been very numerous and their activity undisturbed for long periods of time. When the water of the basin cooled, carbon dioxide escaped, and the precipitation of calcite-, dolomite-, and siderite-bearing muds started; the sediments also contained alternating layers of silica and ferric hydroxide. Additional iron was produced by normal weathering. Sometimes ferrous carbonate was precipitated under reducing conditions, and it was later metamorphosed by hydrothermal solutions under the production of jaspilites and ferruginous cherts. Sometimes silica was leached out and magnetite deposited in its place. In their present shape the oxides connected with volcanic phenomena consist of calcitic and dolomitic limestones, sideritic shales, and jaspilites. In some deposits extensive silicification has been caused by hydrothermal solutions. Many of these formations contain high-grade magnetite and hematite ores.

The iron ores of marine origin may also consist of iron silicates, which sometimes form deposits of technical importance. When the substances present in sea water react with one another or with bottom sediments, a number of minerals will be produced, which occur in recent terrigenous sediments. Some iron-rich silicate minerals are important ore minerals of iron. The chemical reactions caused by sea water are called halmyrolysis, and the minerals formed thereby include, among others, the following:

Glaucinite, $K_{2-3}(Mg, Fe^{2+}, Ca)_{1-3}(Fe^{3+}, Al)_3[(OH)_8 | Al_2-3Si_{13-14}O_{40}]$

Greenalite, $Fe_3^{2+}Fe_3^{3+}[(OH)_6 | Si_4O_{11}]_2 \cdot 2H_2O$

Chamosite, $(Fe^{2+}, Mg)_3[Al_2Si_2O_{10}] \cdot nH_2O$ (?)

These minerals are considered to be formed only in the marine environment.

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The structures of glauconite and chamosite consist of superimposed two-dimensional sheets of $[\text{SiO}_4]$ tetrahedra; but greenalite, a member of the chrysotile group, has $[\text{SiO}_3]$ chains in its structure. Glauconite is structurally almost completely identical with the micas.

Greenalite and chamosite are technically important. Glauconite is the most common iron silicate of sedimentary origin. Its manner of formation was discussed in chapter 12.

The origin of the oxide ores of iron is presented in Figure 33.1 on the basis of Landergren's (1948) diagram.

COBALT, NICKEL

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

COBALT and nickel are members of the iron family (Goldschmidt, 1929) or the ferrides (Landergren, 1943). They are the closest relatives of iron in the Periodic System. Their abundance in the meteorite phases and in igneous rocks is presented in Table 34.1. The meteorite values are those which Goldschmidt (1937*b*) considers to be the most reliable. With reference to the abundance of cobalt and nickel in igneous rocks, the values recorded in Table 34.1 afford proof of considerable discrepancy among those adopted by various authorities. Owing to the great number of ultrabasic rocks included in the material analyzed, van Tongeren (1938) considers his own averages too high. The values given by Sandell and Goldich (1943) are used in this book. Lundegårdh (1946) thinks that Goldschmidt's value for nickel (100 g/ton) is too high. The Swedish rocks analyzed by Lundegårdh yielded a Co:Ni ratio of approximately 1:1.

Both nickel and cobalt are very strongly concentrated in the metal phase of meteorites. However, their solubility in metallic iron is not unlimited, and there is a break in the series of the solid solutions. The nickel-iron occurs as two separate meteorite minerals, viz., kamacite and taenite, which have different nickel contents. The sum of cobalt and nickel in the nickel-iron varies according to the mutual relationships of the two mineral constituents. Geochemically, cobalt and nickel are very pronouncedly siderophile, and their bulk is always found in metallic iron when such a phase is present in the physicochemical system in question. However, as pointed out by Goldschmidt and Peters (1932*b*), cobalt is notably less siderophile than nickel.

The values presented in Table 34.1 show that the content of cobalt and nickel in the sulfide phase of meteorites is remarkably low. Varying amounts of schreibersite, $(\text{Fe,Ni,Co})_3\text{P}$, are nearly always present in the troilite nodules, but the content of cobalt and nickel in the

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pure sulfide phase is rather low. However, the observations on the occurrence of cobalt and nickel in the upper lithosphere show that the two metals possess an unmistakable chalcophile tendency. They combine readily with sulfur and therefore occur as common constituents of sulfide segregations. The low content of cobalt and nickel in troilite is readily explained by studies of the ternary system Fe-Ni-S. It has been found that mixtures having a bulk composition which corresponds to that of meteoritic iron can yield as a stable combination during the crystallization only a mixture consisting of iron monosulfide, FeS, which is nearly totally devoid of nickel, and an iron-

TABLE 34.1
ABUNDANCE OF COBALT AND NICKEL

MATERIAL	Co	Ni	Co:Ni
	g/ton		
Nickel-iron of meteorites (Goldschmidt, 1937 <i>b</i>)	5,700	84,900	0 07
Troilites (Goldschmidt and Peters, 1933 <i>b</i>)	100	1,000	0 10
Silicate meteorites (Goldschmidt, 1937 <i>b</i>)	400	3,300	0.12
Igneous rocks (Vogt, 1923)	8	93	0 09
Igneous rocks (Goldschmidt, Witte, and Hörmann; in Goldschmidt, 1937 <i>b</i>)	40	100	0 40
Igneous rocks, Dutch East Indies (van Tongeren, 1938)	40	126	0 32
Igneous rocks (Sandell and Goldich, 1943)	23	80	0 29
Igneous rocks (Landergrén, 1943)	20	200	0 10
Igneous rocks (Lundegårdh, 1946)	80	48	1 67

nickel alloy. Therefore, the sulfide phase of the meteorites cannot contain considerable amounts of nickel as sulfide but only inclusions of nickel-iron or nickel-bearing schreibersite.

Along with their siderophile and chalcophile character, cobalt and nickel possess an obvious lithophile tendency, because they are frequent constituents of silicate rocks.

It must be emphasized that the Co:Ni ratio in igneous rocks is higher than the ratio in any meteorite phase. This is evidently due to the fact that in acidic rocks cobalt is strongly enriched in relation to nickel (see Table 34.2). In like manner the ratio in the solar atmosphere is in excess of that in the meteorites.

COBALT AND NICKEL IN MAGMATIC SULFIDES

The high affinity of cobalt and nickel for sulfur is the cause of their frequent occurrence in various sulfide bodies segregated from mag-

mas. Nickel is one of the typical constituent elements of the early magmatic sulfide segregations of the pyrrhotite-pentlandite assemblage. Nickel found therein is first separated as mix-crystals of pentlandite, $(\text{Fe}, \text{Ni})_9\text{S}_8$, and pyrrhotite, FeS . At a later stage, pentlandite forms intergrowths with pyrrhotite, and only seldom, when the $\text{Ni}:\text{Fe}$ ratio is very high, is pure pentlandite separated. Pentlandite contains 22–33 per cent Ni and is geochemically and technically the most important nickeliferous sulfide mineral. Nickel preponderates over cobalt in the early segregations. According to Vogt (1923), the $\text{Co}:\text{Ni}$ ratio in the early magmatic sulfides of the nickel ores is 0.08.

Cobalt is not incorporated in pentlandite but occurs concealed in the pyrrhotite structure. According to Berg and Friedensburg (1944), the $\text{Co}:\text{Ni}$ ratio in pyrrhotite varies from 0.02 to 0.07. On the other hand, considerable cobalt but very little nickel enters into pyrite, which crystallizes from the sulfide melt at a late stage.

According to Noddack and Noddack (1931*a*), the average content of cobalt and nickel in primary magmatic sulfides is 2,100 g/ton Co and 31,400 g/ton Ni. The $\text{Co}:\text{Ni}$ ratio is therefore 0.07. However, as pointed out in chapter 5, the composite sample analyzed by Noddack and Noddack probably does not give the true average composition of the sulfides. The $\text{Co}:\text{Ni}$ ratio is close to the value obtained by Vogt (1923), but, according to Table 34.1, the ratio in igneous rocks is very considerably higher. Therefore, it is evident that more cobalt than nickel remains in the silicate phase during the separation of a sulfide melt from a silicate melt, and consequently the sulfide phase becomes impoverished in cobalt. Metallurgical experience also shows that cobalt is much more likely to go into the slag than is nickel. Cobalt, on the other hand, is more plentiful than nickel in late magmatic sulfides. Thus, for example, many metalliferous veins and sulfides of metasomatic origin, genetically connected with granitic rocks, contain more cobalt than nickel. In hydrothermal sulfides the $\text{Co}:\text{Ni}$ ratio is greater than 1:10, often even greater than 1:1, and thus cobalt may predominate over nickel (Berg and Friedensburg, 1944). Generally speaking, cobalt has a considerably higher tendency to remain in residual melts and solutions during magmatic differentiation than nickel has.

Nickel predominates in all pyrrhotites, but in pyrites, independent of their temperature of formation, the content of cobalt is higher than that of nickel. In pyrites from metalliferous veins the $\text{Co}:\text{Ni}$ ratio may be as high as 830 (Berg and Friedensburg, 1944). Cobalt substi-

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tutes for iron in the pyrite structure. It may also be incorporated in sphalerite. According to Oftedal (1940), sphalerites formed at very high temperatures are rich in cobalt. However, there seem to be numerous exceptions to the general rules of the abundance of cobalt and nickel in sulfide minerals and sulfide deposits, and also other than crystal chemical principles rule over the distribution of cobalt and nickel therein (Gavelin and Gabrielson, 1947).

Pentlandite is, with few exceptions, the only independent nickel mineral found in early magmatic sulfide ores. In the late magmatic sulfide segregations, particularly in the metalliferous veins, cobalt and nickel form a number of sulfide and arsenide minerals. The most important species are the following:

Cattierite,	CoS_2
Linnaeite,	Co_3S_4 (51 per cent Co)
Cobaltite,	CoAsS (35.4 per cent Co)
Safflorite,	CoAs_2
Glaucodot (danaite),	$(\text{Co},\text{Fe})\text{AsS}$
Smaltite,	CoAs_{3-2} (about 28 per cent Co)
Skutterudite,	CoAs_3
Niccolite,	NiAs (43.9 per cent Ni)
Breithauptite,	NiSb
Millerite,	$\gamma\text{-NiS}$
Vaesite,	NiS_2
Bravoite,	$(\text{Ni},\text{Co},\text{Fe})\text{S}_2$
Gersdorffite,	NiAsS (up to 35.4 per cent Ni)
Ullmannite,	NiSbS
Rammelsbergite,	NiAs_2
Chloanthite,	NiAs_{3-2} (28.1 per cent Ni)

There are, in addition, other sulfides and sulfoalts of cobalt and nickel, many of which contain antimony and bismuth.

Along with pentlandite, niccolite and chloanthite are important ore minerals of nickel. Millerite and bravoite are mostly found as alteration products in the superficial parts of nickel ores. Millerite is also found in the weathering zone of nickel-rich rocks. Along with the cobalt minerals listed above, cobaltiferous pyrite and pyrrhotite are used as technical sources of this metal.

A number of minerals are found as weathering and reaction products in the oxidation zone of cobalt and nickel ores; among others, the following:

Stainierite,	$\alpha\text{-CoOOH}$
Heterogenite,	$\text{Co}(\text{OH})_2 + \text{Co}(\text{OH})_3$
Sphero-cobaltite,	CoCO_3
Bieberite,	$\text{Co}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$
Erythrite,	$\text{Co}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$
Bunsenite,	NiO
Zaratite,	$\text{Ni}_3[(\text{OH})_4 \text{CO}_3] \cdot 4\text{H}_2\text{O}$
Morenosite,	$\text{Ni}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$
Annabergite,	$\text{Ni}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$

Heterogenite and stainierite are of local importance as ore minerals of cobalt.

COBALT AND NICKEL IN IGNEOUS ROCKS

Like magmatic sulfides, the normal igneous rocks of the main stage of magmatic crystallization are regularly cobalt- and nickel-bearing. The studies of Newhouse (1936) and Ramdohr (1940) showed that igneous rocks contain, as a rule, small quantities of common sulfide minerals, such as pentlandite, pyrrhotite, and pyrite. Therefore, it is evident that these minerals form the seat of a part of the cobalt and nickel present in igneous rocks. However, the bulk of cobalt and nickel found in igneous rocks is incorporated in silicate minerals, being concealed in their structures. If no sulfide minerals are present, the silicates carry all the cobalt and nickel of the rock. This manner of occurrence is of considerable importance for the geochemistry of the two metals in the upper lithosphere. Although cobalt and nickel for technical purposes nearly always are obtained from sulfide-ore bodies, the amounts in question are quantitatively rather unimportant compared with the quantities incorporated in structures of silicate minerals. Therefore, cobalt and nickel are oxyphile in the upper lithosphere.

According to Landergren (1948), titaniferous iron ores contain, on an average, 200 g/ton Co and 300 g/ton Ni. The Co:Ni ratio is 0.67. Cobalt and nickel are, accordingly, enriched in these ores.

Cobalt forms no independent minerals in igneous rocks, but nickel is sometimes found in basic, and in particular in ultrabasic, rocks as the iron-nickel alloys awaruite and josephinite; the nickelian chrysotile garnierite, $(\text{Ni,Mg})_6[(\text{OH})_6|\text{Si}_4\text{O}_{11}]\cdot\text{H}_2\text{O}$; various nickelian chlorites, e.g., the nickelian antigorite nepouite, $(\text{Ni,Mg})_6[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$; and the nickel spinel trevorite, NiFe_2O_4 . The silicate minerals of nickel are, both structurally and chemically, closely related to the corresponding magnesium minerals and usually occur connected with them. However, all these minerals are relatively rare, and only garnierite, with 15–33 per cent Ni, has importance as an ore mineral of nickel.

The content of cobalt and nickel in the various classes of igneous rocks is given in Table 34.2. The values show that nickel is strongly enriched in ultrabasic rocks, whereas the content of cobalt attains a maximum in silicic rocks. This fact is further elucidated by the Co:Ni ratios of the various rock classes. However, the results of Sahama (1945*b*) and Lundegårdh (1946) show that the contents of cobalt and of nickel in acidic rocks are of the same degree of magnitude.

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The ionic radii of the metals considered above are given in the accompanying tabulation.

Ion	Radius (kX)
Mg ²⁺	0.78
Ni ²⁺	0.78
Fe ²⁺	0.83
Co ²⁺	0.82

In acidic rocks the content of both ferrous iron and magnesium is considerably lower than in basic rocks. In addition, magnesium, in relation to ferrous iron, is more strongly impoverished in acidic rocks.

TABLE 34.2

CONTENT OF COBALT AND NICKEL AND THE Co:Ni RATIO IN IGNEOUS ROCKS

Rock	Co	Ni	Co:Ni
	g/ton		
Peridotite (dunite; Goldschmidt, 1937a)	237	3,160	0.08
Gabbro (Goldschmidt, 1937a)	79	158	0.50
Diorite (Goldschmidt, 1937a)	32	40	0.80
Granite (Goldschmidt, 1937a)	8	2.4	3.33
Nepheline syenite (Goldschmidt, 1937a)	8	2.4	3.33
Subsilicic rocks (Sandell and Goldich, 1943)	32	97	0.33
Silicic rocks (Sandell and Goldich, 1943)	3.0	5.8	0.52
Basement Complex of southern Lapland (Sahama, 1945b):			
Ultrabasics	237	~790	~0.30
Gabbros and dolerites	24	47	0.51
Granites	0-8	2-8	max. 4.00
Syenites	8	8	1.00
Basic rocks (Lundegårdh, 1946)	56	65	0.86
Acidic rocks (Lundegårdh, 1946)	11	8	1.38

In like manner, both cobalt and nickel are plentiful in basic rocks and impoverished in the silicic ones, and the abundance of cobalt in the latter rocks increases at the expense of that of nickel. It is evident that nickel replaces magnesium diadochically in mineral structures and becomes enriched therewith. According to previous belief, cobalt prefers the company of ferrous iron. However, Sandell and Goldich (1943) established no linear relationship between the content of nickel and that of magnesium, whereas they found that cobalt varies linearly with magnesium over a wide range of concentrations. They stated that a relation between cobalt and magnesium is more apparent than one between cobalt and ferrous iron. In similar manner

Landergren (1948) found it very unlikely that the ionic radii should regulate the rate of introduction of cobalt and nickel and the Co:Ni ratio in the structures of ferromagnesium minerals. Cobalt and nickel will probably enter any structure of ferromagnesium minerals formed at a certain moment during the crystallization, and other factors than ionic size may cause the changes observed in the Co:Ni ratio with progressive crystallization.

At any rate, nickel has a tendency to become enriched in the early-crystallized magnesium and ferromagnesium minerals. Vogt (1923) found that olivine and hypersthene are the main seats of nickel among the minerals of igneous rocks. Considerably lower nickel contents are found in augite, amphibole, and biotite. The content of nickel varies in relation to the content of olivine and hypersthene in the rocks. In olivine and orthorhombic pyroxene the content of nickel runs parallel to that of magnesium. Olivine may contain up to 0.5 per cent Ni, amphibole and biotite two-tenths of 1 per cent. In granites, nickel is almost quantitatively contained in biotite. The feldspars and the feldspathoids are devoid of this metal.

CYCLE OF COBALT AND NICKEL

Although cobalt and nickel are geochemically closely related elements, they differ with respect to their manner of occurrence in igneous rocks, as the above-presented discussion showed. A corresponding difference also exists in their geochemical cycles. Unlike nickel, cobalt passes into the trivalent state with considerable ease. According to Fersman (1939), the co-ordination number of trivalent cobalt is always 6, whereas the co-ordination number of bivalent cobalt is usually 6 but sometimes 4. In this respect cobalt differs sharply from nickel, which in its compounds in Nature is always bivalent and 6-co-ordinated, and from iron, which in the bivalent state has the co-ordination number 6 and in the trivalent state the co-ordination numbers 4 and 6.

During the weathering, nickel remains largely in the solid products of disintegration and is deposited in the hydrolyzate sediments. Contrary to Fe^{2+} and Mn^{2+} , Ni^{2+} is very stable in aqueous solutions and is accordingly able to migrate for considerable distances under proper circumstances. During the weathering of ultrabasic rocks, particularly of serpentinites, nickel forms a number of hydrosilicates with complicated chemical composition which structurally consist of endless two-dimensional sheets. They form the group of the nickelian chlo-

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rites. Moreover, there are nickel-bearing silicates, e.g., pimelite, $(\text{Ni,Mg})_3[(\text{OH})_2|\text{Si}_4\text{O}_{10}]\cdot n\text{H}_2\text{O}$, which are related to clay minerals and are of a similar origin. Such nickel silicates are sometimes found in peat in soils derived from serpentine rocks.

During the weathering of nickel-bearing silicate minerals the nickel may sometimes accumulate to form veins consisting of pure nickel silicates. Serpentine rocks derived from dunite are likely to be especially rich in nickel. During the lateritic weathering of serpentine, nickel becomes enriched in the insoluble residue, e.g., in the laterite ores of Celebes and Cuba. Serpentine is first converted into magnesite by the carbon dioxide-bearing weathering solutions; but magnesite goes into solution as magnesium bicarbonate in the uppermost weathering zone, and only silica, hydrosilicates of nickel and magnesium, and iron oxide remain as a residue. Nickel often predominates in the hydrosilicates over magnesium.

The transfer percentage of nickel (see Table 6.19) is very small. This shows that only a negligible part of the nickel liberated during weathering and transported into the sea remains in sea water. The bulk is retained in the solid products of weathering. The content of nickel in sediments and their derivatives is shown in Table 34.3. The values show that nickel is enriched in hydrolyzate sediments. According to Maliuga (1939), the content of nickel in bog ores may be as high as 0.4 per cent Ni and in oolitic iron ores up to 3.9 per cent. A very considerable enrichment has occurred in these rocks.

Cobalt does not form hydrosilicates during the weathering. It remains in the weathering solutions as bicarbonate or colloidal hydroxide. It is often separated from nickel and is deposited, along with manganese, in the cobaltian wad (asbolan), which contains from 4 to 34.5 per cent Co, and in other manganiferous oxidates. However, the separation of nickel and cobalt is not complete. During the weathering of the cobalt- and nickel-rich serpentine rocks of New Caledonia, nickel accumulates in garnierite in the zone of weathering and cobalt is carried forth in solution to be deposited in asbolan. The Co:Ni ratio in garnierite is 0.01 and in asbolan 2–5. There also is an excess of cobalt and a deficiency in nickel in bog iron ores and in marine siderite ores. In laterite and in oolitic iron ores both cobalt and nickel have become enriched. This shows that ferrides may become appreciably concentrated in environments favorable for the enrichment of iron in the minor cycle (Landergren, 1948).

In sea water the content of cobalt, like that of nickel, is very low;

and the small value of the transfer percentage shows that cobalt is also almost completely removed from sea water, being deposited in hydrolyzate sediments. Small amounts of cobalt and nickel are also present in sulfides found in marine sediments. Cobalt is, in addition, removed by adsorption in the oxidate sediments. The values presented in Table 34.3 show that nickel usually preponderates over cobalt in the hydrolyzates, but in oxidates the case is the reverse.

TABLE 34.3
CONTENT OF COBALT AND NICKEL AND THE Co:Ni RATIO
IN SEDIMENTS AND THEIR DERIVATIVES

Rock	Co	Ni	Co:Ni
	g/ton		
Mississippi silt, composite (Clarke, 1924)		134	
Terrigenous clays, composite (Clarke, 1924)		498	
Red clay, composite (Clarke, 1924)		253	
Laterite-bauxite ore (Landergren, 1948)	300	180	1.67
Bog iron ores, Finland (Landergren, 1948)	130	40	3.25
Marine oolitic-siliceous iron ores (Landergren, 1948)	200	200	1.00
Marine siderite ores (Landergren, 1948)	300	50	6.00
Glauconite (Palmqvist, 1935)		8	
Sandstone, Västergötland, Sweden (Lundegårdh, 1946)	1.0	2.0	0.50
Shale, Västergötland, Sweden (Lundegårdh, 1946)	60	150	0.40
Bituminous schist, Västergötland, Sweden (Lundegårdh, 1946)	30	70	0.43
Limestones, Västergötland, Sweden (Lundegårdh, 1946)	<0.3-2.0	3.0-10	<0.03-0.70
Quartzites, southern Lapland (Sahama, 1945b)	0	2-8	0
Aluminum-rich schists, southern Lapland (Sahama, 1945b)	8	24	0.33
Carbonate rocks, southern Lapland (Sahama, 1945b)	0	0	

According to Goldschmidt (1937b), the average Co:Ni ratio in hydrolyzate sediments is 0.40. The reason for this low value is that relatively much material derived from subsilicic igneous rocks is incorporated in the hydrolyzates. Although the relationship between cobalt and iron in igneous rocks seems to be indistinct, cobalt rather than nickel accompanies iron in sediments. Thus the pyrites present in shales show a rather strong accumulation of cobalt, just like the hydrothermal pyrites (Goldschmidt, 1937a).

The high affinity of cobalt and nickel for sulfur is further reflected by the fact that the two metals, under reducing conditions, show a tendency to become concentrated in muds rich in organisms and their remains, being precipitated as sulfides in such sediments.

The behavior of cobalt and nickel during metamorphism is not

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well known. During serpentinization, nickel enters into serpentine and talc, the latter of which may contain 0.5 per cent NiO.

COBALT AND NICKEL IN THE BIOSPHERE

Small amounts of cobalt and nickel are widely distributed in plants and animals. In plants the highest nickel concentration is found in the leaves. Both cobalt and nickel are reported in coal ashes, and they may become enriched therein (Goldschmidt and Peters, 1933c). So far, the question of the significance of cobalt and nickel to plants has not been settled, but cobalt, in spite of its low content in biological material, is essential to animals. The deficiency of cobalt in soil and herbage is the established cause of a certain disease ("bush sickness") in grazing animals. Cobalt appears to be essential in the bacterial processes connected with digestion that take place in the rumen of the cow and the sheep. According to Mitchell (1944), the content of cobalt in soil is up to 300 g/ton and that of nickel varies from 5 to 2,000 g/ton; Maliuga (1939) gives a content of 5–10,000 g/ton Ni.

Linnaeite and millerite are frequently met in coal seams and are deposited from percolating solutions. According to Maliuga (1939), coal may contain up to 220 g/ton Ni.

The content of nickel in petroleum and its derivatives may be surprisingly high. Wells (1946) reports a content of 3,000 g/ton Ni in a sample of liquid asphalt, and, according to Maliuga (1939), the content in oil is 1–250 g/ton Ni. Usually, nickel evidently is concentrated in the paraffin hydrocarbons during the polymerization of the oil, in contradistinction to vanadium, which becomes enriched in asphalt. Nickel, like vanadium and molybdenum, forms organometallic compounds in petroleum (see chap. 25), and these are able to migrate with the hydrocarbons. The three metals may have been active as catalysts in the reactions between organic substances and hydrogen sulfide (Goldschmidt, 1937a).

An organic compound of cobalt, julienite, $\text{Na}_2\text{Co}[\text{CSN}]_4 \cdot 8\text{H}_2\text{O}$, occurs in some cobalt deposits at Katanga in the Belgian Congo.

ORES OF COBALT AND NICKEL

Many nickel deposits occur in serpentine rocks. The pyrrhotite-pentlandite deposits are usually associated with norites and less commonly with peridotites. Deposits found in more acidic rocks are of very low grade. Metalliferous veins carrying cobalt and nickel usually contain arsenic along with sulfur (cobaltite, chloanthite, niccolite)

and are associated with diabases and other basic rocks. In deposits associated with silicic igneous rocks, usually little or no cobalt and nickel is present. The nickel-bearing cobalt-uranium-silver veins form an exception to this rule; they are connected with granites. Vogt (1923) emphasized the fact that one of the most important factors which determine the content of nickel in pentlandite-pyrrhotite deposits is the nickel content of the ferromagnesium silicates in the parent-rock. The percentage of nickel in the segregated sulfides increases with the increasing content of nickel in the silicate minerals of the parent-rock.

Garnierite occurs only as a weathering product of peridotites and of serpentine rocks derived therefrom. The garnierite deposits of New Caledonia are the greatest nickel deposits known to occur in the weathering zone.

THE PLATINUM METALS

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

ACCORDING to their position in the Periodic System, the platinum metals are usually divided into two subgroups, viz., (1) the light platinum metals: ruthenium, rhodium, palladium, and (2) the heavy platinum metals: osmium, iridium, platinum.

Like the rare-earth metals, particularly yttrium and the lanthanides, the platinum metals form a geochemically rather coherent group of elements. They are nearly always found to accompany one another in Nature because the atomic volumes of the elements in the two subgroups are nearly equal, a result of the lanthanide contraction (see chap. 5).

The general geochemical character of the platinum metals is illustrated by the abundance numbers given in Table 35.1, based on the values considered by Goldschmidt (1937*b*) to be the most reliable ones. The values were obtained from analyses carried out by Noddack and Noddack (1931*b*) and by Goldschmidt and Peters (1932*b*). The abundance of the platinum metals in the Sun's atmosphere, as given in Table 2.3, is also quoted in Table 35.1. All the values presented show that the rule of Oddo and Harkins is valid for both groups of platinum metals, just as it is for the lanthanides. Rhodium and iridium, which have odd atomic numbers, are less abundant than their even-numbered neighbors.

However, the values recorded in Table 35.1 cannot be considered final. Some of them might be too high, perhaps by a factor of 2 or 3 (Goldschmidt, 1937*b*). It should also be noted that the abundance of ruthenium and osmium in the upper lithosphere is still unknown.

The values presented in Table 35.1 show that the platinum metals are strongly and distinctly siderophile. This feature is the most prominent one, as far as their general geochemical character is considered. It is evident that by far the greatest part of the platinum metals in the Earth is enriched in the nickel-iron core, in which these metals

THE PLATINUM METALS

are dissolved in iron. Only a negligible part has reached the lithosphere. However, considerable quantities of ruthenium and osmium, especially, are present in the sulfide phase of the meteorites. This fact and the occurrence and content of the platinum metals in various sulfide minerals suggest that, in particular, palladium but also ruthenium, platinum, and osmium are chalcophile. However, their chalcophile character is evidently not so pronounced as their siderophile nature, even though palladium is rather strongly chalcophile. In sulfide-ore deposits palladium usually predominates among the platinum metals, but in other occurrences it is much inferior to platinum.

TABLE 35.1
ABUNDANCE OF THE PLATINUM METALS

Z	Element	Sun's Atmosphere (mg·m ⁻²)	Nickel- Iron (g/ton)	Troilite (g/ton)	Silicate Meteorites (g/ton)	Upper Lithosphere (g/ton)
44..	Ru	0 5	10	9	(0)	present
45..	Rh	0 03	5	0 4	(0)	0.001
46..	Pd	0 13	9	2	(0)	0 01
76..	Os	0 06 (?)	8	9	(0)	present
77..	Ir	0 01 ?	4	0 4	(0)	0 001
78..	Pt	0 7	20	2	(0)	0.005

The schreibersite of the iron meteorites also contains platinum metals, but the content is very much lower than in the metal phase.

In the presence of a metal phase and a sulfide phase, the platinum metals, being siderophile, preferentially enter the former. If the metal phase is replaced by a silicate phase, these metals are concentrated in the sulfide. This shows that their lithophile character is very weak.

THE PLATINUM METALS IN IGNEOUS ROCKS

The platinum metals are the most typical among the noble metals. They are found in Nature chiefly in the native state, almost always associated with one another. The composition of their natural alloys shows a considerable degree of variation, and the alloys often form more or less continuous series, in which no sharp limits exist between the various minerals. The natural alloys are listed in Table 35.2.

Usually the platinum metals contain varying quantities of gold, silver, copper, iron, nickel, chromium, and other metals. The most

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important minerals formed by the platinum metals with other elements include the following species:

Laurite,	RuS_2
Stibiopalladinite,	Pd_3Sb
Cooperite,	PtS
Braggite,	$(\text{Pt}, \text{Pd}, \text{Ni})\text{S}$
Niggliite,	PtTe_3
Sperrylite,	PtAs_2

On the whole, the number of minerals formed by the platinum metals is low. Cooperite, braggite, and stibiopalladinite are found only in the platiniferous norites of the Bushveld complex in South Africa. Sperrylite and laurite are more widely distributed.

TABLE 35.2
THE NATURAL ALLOYS OF THE PLATINUM METALS

Name	Crystal System	Essential Composition
Platinum (polyxene)	Isometric	Pt
Platiniridium	Isometric	(Ir,Pt)
Iridium	Isometric	Ir
Palladium	Isometric	Pd
Allopalladium	Hexagonal	Pd
Iridosmine (nevyanskite)	Hexagonal	(Ir,Os)
Osmiridium (siserskite)	Hexagonal	(Os,Ir)
Aurosmiridium	Isometric	(Ir,Os,Au)
Porpezite	Isometric	(Au,Pd)
Rhodite	Isometric	(Au,Rh)
Potarite	Isometric	PdHg or Pd_3Hg_2

According to their siderophile properties, the platinum metals are enriched in native iron separated from basaltic magmas. Goldschmidt and Peters (1932b) found 0.5 g/ton Ru, 0.5 g/ton Rh, 1 g/ton Pd, and 5 g/ton Pt in the iron from Uivfaq, Greenland.

The reluctance of the platinum metals to combine with other elements and their high melting points are responsible for their preferential enrichment in the early-separated fractions during magmatic crystallization. Thus, for example, dunites, pyroxenites, and serpentinites often contain considerable quantities of the platinum metals. In the ultrabasics the platinum metals are frequently concentrated in chromite; and ruthenium and rhodium in particular, which are conspicuously weakly represented in the platinum ores proper and in platiniferous sulfides, are often concentrated in chromite. Gold-

schmidt and Peters (1932*b*) reported up to 0.5 g/ton Ru, 0.5 g/ton Rh, 5 g/ton Ir, and 1 g/ton Pt in chromite. However, native platinum and the various alloys are also found in ultrabasic rocks, as well as the minerals listed above. The silicate minerals are nearly or completely free of platinum metals.

According to Schneiderhöhn and Moritz (1939), the sulfide pyroxenites of the Transvaal in South Africa contain the bulk of the platinum metals in their sulfide minerals. The early-separated pyrrhotite and nickelian pyrite contain the major part, up to 10–50 g/ton, whereas the pentlandite, which is younger, is lower in the platinum metals, and chalcopyrite, the sulfide mineral last to separate, is completely devoid of these metals. Similarly, the platinum metals are usually absent in chromite and in the various silicate minerals; if present, they never exceed 1 g/ton. No independent platinum minerals occur in the unweathered pyroxenites; sperrylite is probably formed in the zone of oxidation during the weathering of platiniferous sulfides.

The platinum metals are almost completely absent in rocks crystallized during the main stage of differentiation. Already the gabbros are almost regularly devoid of platinum, and no primary platinum deposits are known in rocks more acidic than gabbros and norites. The volatile constituents which become concentrated in the residual melts during the main stage of crystallization are evidently able to retain in the melt a small proportion of the platinum metals originally found in the magma, and such platinum metals as remain become enriched in the late crystallates. The columbate, tantalate, zirconate, and titanate minerals found in many granite pegmatites contain notable quantities of platinum metals. Such minerals include, among others, gadolinite, $\text{Y}_2\text{Fe}[\text{O}|\text{BeSiO}_4]_2$, columbite, $(\text{Fe},\text{Mn})(\text{Cb},\text{Ta})_2\text{O}_6$, tantalite, $(\text{Fe},\text{Mn})(\text{Ta},\text{Cb})_2\text{O}_6$, and ilmenorutile, mixed crystals of rutile and tapiolite. Lunde (1927) has found 0.6 g/ton platinum metals in a tantalite.

Because the platinum metals are chemically rather inert, they may, at least partly, occur in magmatic liquors in the native state, probably forming colloidal solutions.

Determinations showing the content of the platinum metals in igneous rocks are very scarce. Lunde (1927) found up to 0.74 g/ton platinum metals in dunite and 0.29 g/ton in peridotite. According to Goldschmidt and Peters (1932*b*), a norite from the Merensky Reef in the Transvaal, South Africa, contains 0.2 g/ton Pd and 0.2 g/ton

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Pt, ruthenium and rhodium being absent. Leutwein (1939) found 0.2 g/ton Pt and 0.1 g/ton Pd in dunite, and 0.5 g/ton Pt and 0.1 g/ton Pd in pyroxenite. The upper limit for these metals in amphibolites of magmatic origin was similar to the content in dunite, whereas in amphibolites of sedimentogenic origin the content was lower. Consequently, the platinum metals, in some cases at least, may be used to indicate the origin of metamorphic rocks.

As was mentioned above, the platinum metals are also more or less pronouncedly chalcophile. This characteristic is already apparent from their distribution between the metal and the sulfide phases of meteorites; it is most pronounced in the case of ruthenium and osmium. Owing to their chalcophile properties, the platinum metals are often found in sulfide minerals, and, according to the considerations presented in chapter 5, they belong to the sulfophile group of elements. Noddack and Noddack (1931*a*) analyzed a composite mixture of magmatic sulfides (see chap. 5). They found the contents of platinum metals given in the accompanying tabulation. The results show

Element	g/ton
Ru	1
Rh	0.3
Pd	4
Os	0.1
Ir	0.4
Pt	2

that the platinum metals are notably concentrated in the early magmatic sulfides.

Ruthenium, palladium, and platinum are the only members of this group which are known to form sulfide minerals (laurite, cooperite, and braggite). Cooperite is an important constituent of the South African platinum ores. The platinum telluride, niggliite, is very rare and probably of secondary origin. Small amounts of platinum metals are usually met in early-separated magmatic sulfides of the pyrrhotite-pentlandite assemblage. Platinum and often palladium are dominant in such sulfides. The Pd:Pt ratio varies according to the sulfide body in question. In many cases palladium predominates over platinum, and the Pd:Pt ratio is usually 2-3 (Goldschmidt, 1926). The considerable abundance of palladium in the sulfides discussed was previously considered a proof of the chalcophile character of this metal. Today it is held that the siderophile character is also the more dominant in the case of palladium. The early-separated sulfides

often contain platinum as sperrylite, but it is possible that the platinum metals generally form solid solutions in the sulfide minerals filling the vacant spaces in their structures (Schneiderhöhn and Moritz, 1939).

Many pneumatolytic and hydrothermal tin ores (cassiterite and stannite) formed during the late magmatic stages contain platinum metals. Thus pneumatolytic cassiterites genetically connected with granitic magmas carry at least platinum (Goldschmidt and Peters, 1932*b*), and in the associated molybdenites the content of platinum and palladium may be considerable (up to 1 g/ton Pt, along with other platinum metals). The presence of platinum in triplite has also been reported: 0.2 g/ton Pt, according to Goldschmidt and Peters. The occurrence of palladium and platinum in molybdenite is readily explained by crystal chemical reasoning: the disulfides of these metals have structures similar to that of molybdenite, and they are isomorphic with this mineral. Palladium and platinum are also distinctly concentrated in hydrothermal nickel and cobalt arsenides. The arsenides, antimonides, and bismuthides are more metal-like than are the sulfides, and this explains why many siderophile elements apparently tend to become concentrated in such compounds during a distribution between a sulfide phase and an arsenide (antimonide) phase. This is in accordance with the observation that the platinum metals crystallize from sulfide melts as minerals like sperrylite and stibiopalladinite.

The hydrothermal sulfosalts, e.g., tetrahedrite and bournonite, may contain small quantities of platinum metals, but silver predominates in such minerals. Platinum has also been reported to occur in galena. What is left of the platinum metals after the separation of hydrothermal sulfides and other minerals crystallizes in the native state in quartz veins.

CYCLE, ORES, AND BIOGEOCHEMISTRY OF THE PLATINUM METALS

According to Schneiderhöhn and Moritz (1939), the platinum metals are dissolved during the weathering of platiniferous sulfides. With the exception of palladium, which is partly removed, they are readily reprecipitated in the zone of oxidation and may become enriched to form independent minerals, e.g., sperrylite and cooperite. During prolonged oxidation and weathering, the platinum metals are separated in the native state. Thus, for example, sperrylite is decom-

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posed to native platinum and arsenic trioxide, As_2O_3 . Consequently, most of the platinum metals remain in the resistates, whereby placer deposits may be formed. A small part goes into the sea and is finally deposited in the hydrolyzates and oxidates. However, the platinum metals found in the deep-sea sediments are partly derived from meteoritic dust. The dissolved platinum metals may become considerably enriched in the manganese nodules: Goldschmidt and Peters (1932*b*) report 0.2 g/ton Rh, 0.2 g/ton Pd, and 0.5 g/ton Pt in a nodule.

With the exception of the platinum metals recovered as by-products from various sulfide ores, the greatest part of these metals is obtained from resistate sediments, both recent and ancient; the latter may contain platinum metals along with other heavy minerals enriched in certain horizons. Placer deposits of platinum and associated metals derived from ultrabasic igneous rocks (dunites, pyroxenites, serpentinites) are met in many places, e.g., in the Urals in Russia and in South America. Notable amounts of platinum are mined in South Africa from basic and ultrabasic igneous rocks: norites and iron-rich dunites.

Platinum is reported in the ashes of some marine animals. Rhodium, palladium, and platinum are enriched in coal ashes (see chap. 8).



COPPER

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

COSMICALLY, copper is relatively abundant, as compared with the other heavy metals. Figure 2.2 shows that copper is cosmically as abundant as zinc. The presence of copper has been established in the solar and stellar atmospheres. The general abundance values of copper are presented in Table 36.1. The new copper determinations in igneous rocks have yielded concordant results, but the average

TABLE 36.1
ABUNDANCE OF COPPER

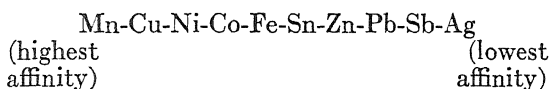
Material	Cu (g/ton)
Metal phase of meteoritic iron (Goldschmidt, 1937b).....	normal: 100-400 maximum: 1,000
Metal phase of stony meteorites (Goldschmidt, 1937b).....	0-3,000
Troilite from meteoritic iron (Goldschmidt, 1937b).....	100-600
Silicate phase of chondrites (Noddack and Noddack, 1930)	1 55
Igneous rocks (Sandell and Goldich, 1943) .	70
Igneous rocks (Lundegårdh, 1946)	60

content of copper in meteorites is still a matter of controversy. The average copper content of the various meteorite phases cannot be readily determined because the amount of copper in the meteorites is subject to wide fluctuations, which are more pronounced than for most other elements. The results show, however, that very little copper, if any, is generally present in the silicate phase, whereas the copper content in the metal phase is reasonably high and the sulfide phase may contain still more copper. Therefore, it is evident that copper, geochemically, is mainly chalcophile, but not without a siderophile tendency. These results are corroborated by the observations concerning the manner of occurrence of copper in the upper lithosphere. It is a well-established fact that copper shows a high affinity for sulfur and is one of the most typical constituents of sulfide

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ores. On the other hand, a little copper is found in native terrestrial iron, and up to 13 per cent copper, along with some other metals, is present in the native platinum metals and in their alloys, being thus incorporated in the native state in a metal phase separated from a silicate phase.

The observations made in copper-ore smelters show that copper, among the sulfide-forming metals, has one of the highest affinities for sulfur. The affinity of metals for sulfur during the smelting of sulfide ores decreases in the following order:



This is the series of Fournet and Schütz. Copper is the second member therein. The values presented in Table 4.1 show that copper, during the smelting of the Mansfeld copper ore, goes into the copper matte, which consists mainly of copper sulfide. Several other metals found in this ore as sulfides, particularly iron but also nickel, cobalt, molybdenum, etc., are separated in the metal phase. The metal showing the highest affinity for sulfur, viz., manganese, is also enriched in the copper matte.

The abundance of copper in igneous rocks is probably higher than indicated because considerable quantities of copper may have been introduced by the late magmatic activity directly to the exogenic cycle (Goldschmidt, 1937b).

COPPER IN IGNEOUS ROCKS; COPPER ORES

The high affinity of copper for sulfur forms the basis of the metallurgical treatment of copper ores. In like manner this property is the factor determining the manner of occurrence of copper in the Earth's crust. Sulfides and sulfosalts are the most important copper minerals, and it is evident that by far the greatest part of copper in the upper lithosphere is bound within these minerals. Consequently, copper belongs to the group of the sulfophile elements, even though its sulfophile character is not very pronounced (chap. 5).

Among the silicate minerals of copper chrysocolla, $\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$, and diopside, $\text{Cu}_3[\text{Si}_3\text{O}_9] \cdot 3\text{H}_2\text{O}$, are the most important species. The former is relatively common, but neither of the two is found as an actual constituent of igneous rocks. Their occurrence is restricted mainly to hydrothermal veins, and therefore they have only slight significance as far as the geochemistry of copper is concerned. Ac-

according to the surveys of Newhouse (1936) and Ramdohr (1940), copper is, chiefly or entirely, present as chalcopyrite, CuFeS_2 , in unaltered normal igneous rocks belonging to the main stage of crystallization, whereas only a smaller amount is found as bornite, Cu_5FeS_4 , and cubanite, CuFe_2S_3 . Like molybdenum, copper thus shows a strong tendency to combine with all available sulfur during the crystallization of rocks. However, the composition of the resulting copper sulfides is more complicated than in the case of molybdenum, which yields only molybdenite, MoS_2 . The copper-iron sulfides mentioned are always the last minerals to crystallize; they fill the interstices between other minerals in igneous rocks.

According to Sandell and Goldich (1943), the average copper content of igneous rocks is the following:

Rock	Cu (g/ton)
Basic igneous rocks	149
Intermediary igneous rocks	38
Acidic igneous rocks	16

Lundegårdh (1946) reports 15 g/ton Cu as the average for acidic rocks and 30 g/ton for basic igneous rocks, but the latter value is evidently too low. The values show that copper tends to become enriched in the basic rocks, which contain about ten times as much copper as do the acidic ones. According to Newhouse (1936), the basic rocks form the locus of most abundant chalcopyrite.

It is probable that small amounts of copper may replace ferrous iron in mineral structures in the absence of an appropriate supply of sulfur, owing either to oxidation or to previous crystallization. The reason for the substitution is the similarity of the radii of Cu^{2+} (~ 0.83 kX) and Fe^{2+} (0.83 kX), and the replacement would take place, e.g., in augites, as suggested by Ramdohr (1940). Carobbi and Pieruccini (1947) suggested that copper replaces Fe^{2+} and Mg^{2+} , for instance, in tourmaline. At any rate, it is evident that the occurrence of copper in silicate and oxide minerals is not very important geochemically, whereas the formation of sulfides is its most characteristic feature.

The foregoing facts show that the rocks formed during the main stage of crystallization are not the proper abode of copper. This metal is found rather regularly as a constituent of the early-separated sulfides, which belong chiefly to the pyrrhotite-pentlandite paragenesis. The series of Fournet and Schütz shows that the affinity of copper for sulfur is higher than that of nickel and iron, the main metallic

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constituents of the early-separated sulfides. Therefore, it follows that, during the separation of the sulfide phase from the silicate phase, copper becomes considerably enriched in the sulfide melt. The part of copper which remains in the silicate melt after the separation of the sulfides stays in residual magmas during the main stage of crystallization and all through the pegmatitic stage, being finally separated in the pneumatolytic and hydrothermal deposits. In the last-mentioned formations copper occurs as a constituent of a great number of sulfides and sulfosalts which show pronounced variations in their composition, manner of occurrence, and paragenesis, usually together with silver, germanium, tin, lead, iron, nickel, cobalt, and still other metals. A number of arsenides, antimonides, selenides, and tellurides of copper are known, in addition. The most important sulfides and sulfosalts of copper are the following:

Chalcocite,	Cu_2S
Bornite,	Cu_5FeS_4
Chalcopyrite,	CuFeS_2
Tennantite,	$\text{Cu}_3\text{AsS}_3-4$ (?)
Tetrahedrite,	$\text{Cu}_3\text{SbS}_3-4$ (?)
Enargite,	Cu_3AsS_4
Cubanite,	CuFe_2S_3
Covellite,	CuS
Bournonite,	$2\text{PbS} \cdot \text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$

The more important constituents of copper ores are included in this list. Chalcopyrite, with 34.6 per cent Cu, is one of the most important sources of copper. Along with the above minerals, the copper ores often contain secondary copper minerals as alteration products. They include native copper, chrysocolla, diopside, and the following species:

Cuprite,	Cu_2O
Brochantite,	$\text{Cu}_4[(\text{OH})_6 \text{SO}_4]$
Chalcanthite,	$\text{Cu}[\text{SO}_4] \cdot 5\text{H}_2\text{O}$
Azurite,	$\text{Cu}_3[\text{OH} \text{CO}_3]_2$
Malachite,	$\text{Cu}_2[(\text{OH})_2 \text{CO}_3]$

Like the sulfides, the secondary minerals of copper also are constituents of many copper-ore bodies of economic importance. A large number of other sulfates and carbonates of copper and its silicates, arsenates, and phosphates of varying and often complicated composition are known as minerals.

CYCLE OF COPPER

During the weathering the superficial parts of the copper-ore bodies are oxidized. The copper-iron sulfides are decomposed, and copper is brought into solution as the stable cupric sulfate, whereas

the ferrous sulfate is oxidized rather rapidly, whereby sulfuric acid and ferric hydroxide are formed. The copper sulfate solutions migrate downward, and at a certain level immediately below the zone of oxidation, but still above the ground-water table, they react with the undecomposed sulfide minerals, and native copper and copper-rich sulfides (e.g., chalcocite and chalcopyrite) are thereby formed. Other copper minerals, e.g., cuprite; tenorite, CuO ; azurite; and malachite, may also be deposited. Consequently, copper becomes enriched in the zone of cementation. In addition, the cupriferous solutions may migrate from the zone of weathering into the surrounding rocks along cracks and fissures and deposit copper as sulfate and carbonate. These minerals are readily observed because of their bright green and blue colors. Vogt and Rosenqvist (1942) found up to 3.2 g/ton Cu in surface waters which have passed through copper mines, open pits, waste-ore dumps, etc. During the weathering of the copper sulfides found in igneous rocks, copper dissolves as cupric sulfate in a similar way. As soon as possible, these solutions deposit copper as sulfide. If the cupriferous solutions are brought into contact with sapropelic muds, the precipitation of copper sulfide may be extensive enough to cause the formation of sedimentary copper ores, such as the bituminous shales found in Germany and in Russia, e.g., the Permian *Kupferschiefer* at Mansfeld in Germany, which contains bornite, chalcocite, and chalcopyrite along with native silver, and zinc and lead minerals. According to Goldschmidt (1937a), these shales may, wholly or partly, owe their existence to the erosion and redeposition of old enriched humus soils. However, according to some more recent views (see e.g., Siegl, 1941), postdiagenetic acid solutions should be responsible for the copper mineralization of the shale. Sometimes copper salts are concentrated in ground waters as a result of profuse evaporation, particularly in arid regions, and copper may then be precipitated, for example, as carbonate, which in sandstones forms the cementing substance between the detrital mineral grains.

To sum up what has been said above, copper goes into ionic solution during the weathering, being afterward largely precipitated as sulfide. Another part of copper is trapped in hydrolyzate sediments by sorption. A third part is removed in the oxidates, e.g., in lake and bog ores and in manganese nodules, together with nickel, cobalt, zinc, lead, and other metals, whereby adsorption compounds like CuMn_2O_5 may be formed. The content of copper in some sediments and sedimentary rocks is presented in Table 36.2.

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A small amount of copper remains in the oceans, but its content therein is kept low, owing to the adsorption on, or possibly combination with, marine organisms. It is probable that copper is brought to the sea partly also by volcanic emanations, which often are cupriferous. Thus, for example, Zies (1924) found 2,300 g/ton Cu in a fumarolic magnetite from the Valley of Ten Thousand Smokes in Alaska. The amount of copper in sea water is too small to lead to the presence of noticeable amounts of copper in marine evaporates. Any cuprous salts brought into the sea are soon oxidized to cupric compounds. The solubility of copper in sea water is limited by that of its oxychloride, which is precipitated and gradually changes into a basic carbonate.

TABLE 36.2

CONTENT OF COPPER IN SEDIMENTS AND SEDIMENTARY ROCKS

Material	Cu (g/ton)
Mississippi silt, average (Clarke, 1924)	34
Terrigenous clays, average (Clarke, 1924)	128
Terrigenous blue mud, average (Siebenthal, 1915)	7
Red clay, average (Clarke, 1924)	160
Italian argillaceous sediments (Carobbi and Pieruccini, 1943)	192
Manganese nodule (Siebenthal, 1915)	3,000
Limestones, average (Siebenthal, 1915)	20.2
Dolomites, average (Siebenthal, 1915)	12.6

BIOGEOCHEMISTRY OF COPPER

Copper possesses definite biophile properties. It is invariably found as a microconstituent of plants and animals. In plants it stimulates the growth when present in small amounts but is poisonous in large quantities. However, some plants are able to concentrate copper; for example, leguminous plants are rich in this metal. Erkama (1947) states that copper in plants may be present entirely as protein complexes. Vogt (1942) and Vogt and Braadlie (1942) have found that *Viscaria alpina* and *Melandrium dioecum* growing in copper-poisoned soil may endure a copper content as high as 6,500 g/ton, the normal content of soil being 20 g/ton Cu. The two plants are consequently able to survive in the neighborhood of outcropping copper-ore bodies, copper mines, etc., where all other vegetation will perish. Copper is also enriched in coal ashes. It is, further, concentrated in some animals, the oysters being exceptionally rich, with a maximum of 60 g/ton Cu in fresh tissue. Harvey (1945) suggests that copper may combine with large organic molecules to form insoluble salts or co-

ordination compounds which are only very slightly dissociated, such as the protein molecules.

Copper is an essential element in the respiratory pigment hemocyanin found in the blood of many marine invertebrates (arachnids, crustaceans, mollusks). It is also present in the ashes of seaweeds and corals. Turacin, a copper porphyrin, is found in feathers. Other natural organic copper compounds include hemocuprin, hemocuprein, and hepatocuprein. Hemocuprein is a copper protein compound which is believed to be a factor in the synthesis of hemoglobin. Copper is also an essential microconstituent in the growth of many grazing animals and an oxidation catalyst in some enzymes which actually are copper-protein complexes.

Although much copper concentrated by marine organisms remains in organic circulation, a considerable proportion must have been deposited during the geological history of the Earth in sediments rich in organic matter. Thus copper becomes enriched in bituminous substances and sapropelic sediments. Native copper found in sediments and peat bogs is believed to be formed by micro-organisms able to reduce cupric sulfate solutions.

SILVER, GOLD

ABUNDANCE AND GEOCHEMICAL CHARACTER

AS IN the case of the platinum metals and copper, very small amounts of silver and gold, if any, are present in silicate minerals constituting the normal igneous rocks. Their abundance in igneous rocks and in the various meteorite phases is presented in Table 37.1, which is based on the values given by Goldschmidt (1937*b*), partly according to Noddack and Noddack and partly according to previous researches of Goldschmidt and Peters. However, some of the

TABLE 37.1
ABUNDANCE OF SILVER AND GOLD

MATERIAL	Ag	Au
	g/ton	
Nickel-iron... ..	4	4
Troilite.....	18	0.5
Silicate meteorites... ..	(0)	(0)
Igneous rocks.....	0.10	0.005

values recorded appear unreliable. As stated by Goldschmidt (1937*b*), the values for igneous rocks might be too high.

Geochemically, silver and gold differ sharply from each other. Silver is strongly enriched in the sulfide phase of the meteorites. This fact and the manner of occurrence of silver in the upper lithosphere afford proof of its typically chalcophile character. Gold, on the other hand, is very pronouncedly concentrated in the nickel-iron. It is true that gold readily accompanies chalcophile elements in the upper lithosphere, but this circumstance is due to the difference in the redox potential in the superficial parts of the Earth and in the meteorites (see chap. 1). With reference to its terrestrial manner of occurrence, gold, contrary to previous belief, is siderophile, being enriched in the

nickel-iron core. It therefore very much resembles platinum in this respect.

The presence of silver has been established in the solar atmosphere, and gold is probably also present therein.

MANNER OF OCCURRENCE IN THE UPPER LITHOSPHERE

Silver, gold, and copper all belong to the same subgroup of the Periodic System. Therefore, the manner of occurrence of silver and gold in the upper lithosphere notably resembles that of copper. Copper and silver are sulfophile and occur mostly combined with sulfur and, partly, with selenium in the form of various sulfides and selenides. Silver forms, in addition, a number of tellurides and sulfosalts, the latter chiefly with copper, germanium, tin, lead, and manganese. In spite of its siderophile character, gold follows copper and silver in the upper lithosphere: it is sulfophile. However, it does not form any independent sulfide minerals. Gold accompanies selenium and, particularly, tellurium and becomes enriched together with these elements. It is found in Nature in the native state, alloyed with silver and the platinum metals, and as tellurides in many sulfide deposits. The tendency of copper and silver to combine with sulfur and the affinity of gold for tellurium is probably partly due to the ionic properties of these elements. Their ionic radii are the following:

Cu^+ , 0.96 kX	S^{2-} , 1.74 kX
Ag^+ , 1.13 kX	Se^{2-} , 1.91 kX
Au^+ , 1.37 kX	Te^{2-} , 2.11 kX

Consequently, one would expect the cation with the greatest radius, Au^+ , preferably to combine with the biggest of the negatively charged ions, viz., Te^{2-} .

Silver and especially gold are enriched in telluric iron separated from basalt: Goldschmidt and Peters (1932b) report up to nearly 10 g/ton Ag and 5 g/ton Au in such irons. Like copper, silver and gold also readily become enriched in sulfides separated during the early stages of magmatic differentiation. In the case of silver, which is geochemically chalcophile, this behavior is rather natural. Gold, on the contrary, affords another example of the general rule, valid for many siderophile elements like the platinum metals and rhenium, that, in the absence of a metal phase, such elements are concentrated in the sulfide phase. However, there are other elements, more or less pronouncedly siderophile, which are carried over to the silicate phase, e.g., phosphorus and tungsten.

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Among the early-separated oxides, only chromite contains gold and silver: Goldschmidt and Peters (1932*b*) report contents of 1 g/ton Ag and 0.2 g/ton Au.

During the main stage of crystallization the content of silver and gold actually present in the separated minerals is probably still smaller than that of copper. Like copper, the two metals are enriched in the late magmatic products. The separation of gold, in particular, often begins prior to that of copper during the pegmatitic stage of crystallization. The pegmatitic and hydrothermal formations are the most characteristic abodes of silver and gold. Minerals genetically connected with pneumatolytic tin deposits may also carry notable amounts of silver and gold, such as cassiterite (up to 0.5 g/ton Au and nearly 100 g/ton Ag, according to Goldschmidt and Peters, 1932*b*), molybdenite (in excess of 100 g/ton Ag, nearly 10 g/ton Au), and triplite. The two metals are often enriched also in pegmatite minerals, such as ilmenorutile, tantalite, and samarskite (Lunde, 1927; Lunde and Johnson, 1928).

With the exception of native silver, which, like native copper, is often of secondary origin, the most important minerals of silver include the following sulfides and sulfosalts:

Argentite and acanthite,	Ag_2S
Stephanite,	$5\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$
Polybasite,	$8(\text{Ag}, \text{Cu})_2\text{S} \cdot \text{Sb}_2\text{S}_3$
Pyrargyrite,	Ag_3SbS_3
Proustite,	Ag_3AsS_3

All the minerals listed are important ore minerals of silver, argentite being probably the most important primary silver mineral. The argentian tetrahedrite (freibergite), $(\text{Cu}, \text{Ag})_3(\text{Sb}, \text{As})\text{S}_{3-4}$ (?) may also be an important ore of silver. Still another argentiferous mineral of technical importance is galena, which may contain up to 2 per cent silver. The galenas formed at high and intermediate temperatures are richer in silver than those crystallized at low temperatures (Oftedal, 1940). The silver content of galena is usually due to the presence of admixed silver minerals separated from the galena structure. Sometimes there occur small amounts of argentite or matildite (schapbachite), AgBiS_2 , which form isomorphic mixtures with galena. Pure sphalerite is always devoid of silver (Oftedal, 1940).

Native silver is never pure; it usually contains gold, copper, and other metals as impurities. Silver also occurs alloyed with mercury as kongsbergite, α -(Ag,Hg), and moschellandsbergite, γ -(Ag,Hg).

The most important gold tellurides are calaverite, AuTe_2 , and sylvanite, AuAgTe_4 . Like native silver, native gold also is always impure. Silver, copper, iron, and the platinum metals are the foremost impurities. The gold amalgam, (Au, Hg) , is rare.

In the simultaneous presence of a sulfide and an arsenide (antimonide) phase, gold, because of its siderophile behavior, is preferentially concentrated in arsenides and antimonides, which possess a pronouncedly metal-like character. Likewise, gold, as a siderophile element, prefers the metal-like minerals of the pyrite and marcasite-loellingite groups. It is generally associated with pyrite and arsenopyrite.

According to Goldschmidt and Peters (1932*b*), silver predominates over gold in most sulfides and sulfosalts found in hydrothermal veins, as in chalcopyrite, bornite, and tetrahedrite, in which the $\text{Ag}:\text{Au}$ ratio is 500–2,000, whereas gold is preferentially concentrated in the hydrothermal cobalt arsenides and especially nickel arsenides. If both chalcopyrite and pyrrhotite (pentlandite) are formed in a sulfide deposit, silver prefers the former. Lunde (1927) reports 11.5 g/ton Ag in the chalcopyrite from Knaben, Norway, and only 4.0 g/ton in the associated pyrrhotite. In late hydrothermal veins gold accompanies quartz, whereas silver minerals are usually found in carbonate veins (van Aubel, 1934). Gold seems to prefer the sodic albite pegmatites connected with acidic and intermediary magmas, whereas tin is found in potassic pegmatites. In the magmatic solutions gold, being chemically rather inert, is at least partly carried as dissolved or colloidal native metal.

No reliable values are available to show the average content of silver and gold in igneous rocks. Lunde (1927) and Lunde and Johnson (1928) found up to 2.1 g/ton Ag in dunite, up to 9.4 g/ton in peridotites, and 0.3 g/ton in eclogite. In eclogite, silver is contained in the garnet, whereas the pyroxene is devoid thereof. Goldschmidt and Peters found 0.5 g/ton Ag in a norite; Wagoner (according to Clarke, 1924) reports 0.5 g/ton Ag in a basalt, 7 g/ton in a diabase, and 0.9–7.7 g/ton in granites. The average found by Goldschmidt (1926) for the alkalic igneous rocks of the Oslo province is 0.12 g/ton Ag. The gold analyses are still scarcer. Leutwein (1939) found 0.1 g/ton Au in pyroxenite, and 0.1–0.2 g/ton in amphibolites of magmatic origin. The value for amphibolites of sedimentary origin was 0–0.1 g/ton. Wagoner found 0.026 g/ton Au in a basalt, 0.076 g/ton in a diabase, and 0.1–1.1 g/ton in granites.

CYCLE OF SILVER AND GOLD

Gold and silver also differ notably from each other in their behavior during weathering. Like copper, silver is brought into solution as sulfate. However, the solubility of silver sulfate is lower than that of cupric sulfate. In the cementation zone of ore deposits, silver is, reprecipitated, usually as the chloride chlorargyrite, AgCl , which is an ore mineral of silver, or as sulfide. Bromides and iodides of silver are similarly found in the upper parts of silver deposits as products of secondary reactions caused by descending waters. The silver-bearing solutions formed during weathering deposit their silver as either sulfide, chloride, or sulfate in the hydrolyzate sediments. Sometimes silver is deposited in sandstones as chloride closely associated with plant fossils and clay galls (Utah, United States). Another example of the action of biological processes in the deposition of silver is afforded by the *Dictyonema* shales of Scandinavia, which may contain several g/ton Ag (Goldschmidt, 1931a). The marine hydrolyzates are sometimes remarkably rich in silver. Goldschmidt (1926) reports the averages given in the accompanying table. These values afford proof

Material	Ag (g/ton)
Norwegian Quaternary clays	0.05
Deep-sea sediments.	0.11
Terrigenous sediments, western coast of South Africa.	0 66

of considerable regional variations in the silver content of various parts of the Earth.

According to Wagoner (quoted by Clarke, 1924), sandstone contains 0.44 g/ton Ag and limestone about 0.2 g/ton. Silver becomes concentrated in marine oxidates also: Goldschmidt and Peters (1932b) found 1 g/ton Ag in a manganese nodule.

Because gold is chemically more inert than silver and because its compounds are readily reduced to metal, it remains largely in the native state and becomes concentrated in the resistates. Owing to its high specific gravity, gold often forms placer deposits with a relatively high gold content. These deposits represent one of the most important types of gold ores. Gold is readily dissolved and transported, probably largely in colloidal solutions, which may deposit it even at low temperatures. Any gold dissolved from gold ores in the zone of oxidation is redeposited in the cementation zone, in which a secondary enrichment may sometimes take place. Only negligible

amounts of gold are carried into the seas; gold is finally removed by adsorption on hydrolyzate sediments. Like silver, gold may become enriched in the oxidates. Wagoner (according to Clarke, 1924) found an average of 0.028 g/ton Au in some sandstones and 0.005–0.009 g/ton in limestones. Goldschmidt and Peters (1932b) report 0.2 g/ton Au in a manganese nodule.

MANNER OF OCCURRENCE IN THE BIOSPHERE

Silver is known as a widely, but very sporadically, distributed microconstituent in various terrestrial and marine organisms. Up to 1.5 g/ton Ag are reported in the ashes of marine algae. Sea water rich in plankton organisms is reported to be particularly high in silver and gold, and it has been suggested that these metals are not present in true solution in sea water but are adsorbed on the surface of marine organisms. Silver is also reported to occur in fungi, and algae are believed to precipitate silver from thermal waters. A maximum of 10 g/ton Ag is reported in coal ashes (see chap. 8), in which silver is consequently considerably enriched. According to Mitchell (1944), the silver content of soil may be as high as 2 g/ton.

Gold is known to become concentrated by certain plants particularly in seeds, but its biological role in plants is unknown. Only few plants seem to be able to concentrate gold. The ashes of *Equisetum* growing in gold-rich areas may contain up to 610 g/ton Au, corresponding to a content of approximately 60 g/ton in the plant. Humus soil contains 0.1–0.5 g/ton Au (v. Thyssen-Bornemisza, 1942). Up to 0.5 g/ton Au may be present in coal ashes. Gold is also found in some marine animals. Fine gold particles derived from sand are sometimes found in the stomachs of birds.

The action of man as a concentrating agent of silver and gold is of geochemical interest. Zviaginzev (1941) has calculated that the concentration of gold in the anthroposphere is already of the order of 0.001 per cent of the total amount of gold in the Earth.

ZINC, CADMIUM

ABUNDANCE AND GEOCHEMICAL CHARACTER

BESIDES being found in the Earth, zinc and cadmium have been detected and quantitatively determined in the solar atmosphere, and the presence of zinc has been established in stellar atmospheres as well. The most recent abundance values of these metals in igneous rocks are calculated for zinc from data given by Lundegårdh (1947) and for cadmium by Sandell and Goldich (1943). The values reported for the meteorites are from Noddack and Noddack (1930, 1934). All these values are given in the accompanying table.

	Zn	Cd
	g/ton	
Nickel-iron	115	8
Troilites...	1,530	30
Chondrites	76	1 6
Igneous rocks	132	0 15

Although these values cannot be considered final, they show that the highest concentrations of the two metals are met in the sulfide phase of meteorites, the second highest values being found in igneous rocks (Zn) and in the metal phase (Cd). The silicate meteorites contain considerably lower quantities of the two metals. It is evident that zinc and cadmium are predominantly chalcophile. In the upper lithosphere they are classified among the oxyphile elements.

MANNER OF OCCURRENCE IN IGNEOUS ROCKS; ORES

In the early magmatic sulfides the amount of zinc and cadmium is relatively low. Sphalerite, the most common and most important of the sulfide minerals of zinc, which also contains a large proportion of all cadmium (up to 4.5 per cent, according to Oftedal, 1940), does

not belong to the pyrrhotite-pentlandite paragenesis. This circumstance is fully in accord with the fact illustrated by the series of Fournet and Schütz (see chap. 36), viz., that the affinity for sulfur of zinc and of the chemically rather closely related cadmium is lower than that of iron, nickel, cobalt, and copper, all of which are found as the main constituents of the sulfide minerals in question. However, the part of zinc and especially cadmium which is separated from the magma contemporaneously with the early sulfides remains in the residual solutions formed during their crystallization and goes into the late differentiates. Therefore, zinc and cadmium are more substantial constituents of those parts of the sulfide ores which were the last to crystallize and which often intrude the surrounding rocks in the form of apophyses. However, Ramdohr (1940) believes that a small part of zinc is found in pyrrhotite, because some pyrrhotites formed at elevated temperatures, e.g., in basalt, contain admixed sphalerite, which probably was originally present as wurtzite. It must also be noticed that troilites may contain as much as 6,000 g/ton Zn (Goldschmidt, 1937b).

Along with cadmium, sphalerite may carry iron, manganese, cobalt, gallium, germanium, indium, and thallium. An extensive literature exists dealing with the minor elements incorporated in sphalerite. These impurities may be used as indicators of the temperature of formation of the sphalerites, although regional causes are also known to be active in determining its composition. As a general rule, the hydrothermal sphalerites formed at high temperatures contain cobalt and much iron and manganese, whereas the content of gallium and germanium is low and thallium is absent. The content of cadmium seems to be relatively independent of the temperature and geological surroundings. Gallium and indium favor sphalerites formed at intermediate temperatures. Low iron and manganese contents afford proof of an intermediate or low temperature of formation; the content of germanium is high in low-temperature sphalerites, and thallium is found only in sphalerites formed under such conditions (Goldschmidt and Peters, 1933a; Graton and Harcourt, 1935; Oftedal, 1940; Stoiber, 1940; Evrard, 1943; Gabrielson, 1945; Warren and Thompson, 1945).

The silicate rocks formed during the main stage of differentiation contain proportionately more zinc than cadmium. The manner of occurrence of zinc is determined by its property of diadochically replacing ferrous iron and magnesium in mineral structures. The radii

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of these ions are: $r_{\text{Zn}^{2+}} = 0.83 \text{ kX}$; $r_{\text{Fe}^{2+}} = 0.83 \text{ kX}$; $r_{\text{Mg}^{2+}} = 0.78 \text{ kX}$. This similarity causes the presence of zinc in magnetite and ilmenite and explains the fact that early magmatic oxide ores are actually weakly zinciferous. Although zinc forms the independent minerals gahnite, ZnAl_2O_4 , and franklinite, $(\text{Zn,Mn})\text{Fe}_2\text{O}_4$, they are not usually found in igneous rocks but occur in metamorphic rocks, being apparently formed in the reaction between zinc sulfide and oxides of other metals. Zinc does not form independent silicate minerals in igneous rocks. No ternary compound is known of the system $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$; and the thermochemical studies of Schiebold (1931) indicate that zinc cannot be normally incorporated in feldspars (see chap. 5); Ottemann (1941) reports a zinc content up to 0.006 per cent in plagioclase of metasomatic rocks. There are local varieties rich in zinc of many minerals of petrological importance, such as amphibole, pyroxene, melilite, tourmaline, garnet, etc., but they have no general geochemical importance. Foshag (1936) reports 4.70 per cent ZnO in a sodic amphibole. Biotite usually shows the highest content of zinc among the common rock-making minerals; the content is lower in phlogopite and still more so in muscovite (Erämetsä, 1945). Bray (1942a) reports as much as 0.24 per cent ZnO in biotite. Along with the amphiboles and pyroxenes, biotite is the main carrier of zinc in normal igneous rocks.

Notwithstanding its relatively great ionic radius, zinc in its compounds is always 4-co-ordinated with respect to oxygen. The reason for this exceptional behavior is still unknown. This manner of occurrence of zinc causes its minerals, in general, to have relatively loosely packed structures. As shown by Fairbairn (1943), the packing index of zinc minerals is always smaller than that of other minerals with corresponding structures. Another remarkable fact in the crystal chemistry of zinc minerals is the isotypy of willemite, $\text{Zn}_2[\text{SiO}_4]$, and phenakite, $\text{Be}_2[\text{SiO}_4]$. It should be noticed that the ionic radius of Be^{2+} (0.34 kX) is less than half the radius of Zn^{2+} .

During the magmatic differentiation, zinc and cadmium, together with many other elements, remain largely in the residual melts and solutions throughout the main stage of crystallization and the pegmatitic stage. Lundegårdh (1948) found the highest zinc contents in the later, more acidic products of differentiation and in such later differentiates as have the highest content of ferromagnesium minerals, especially biotite. He also claimed that the high volatility of some of its compounds tends to concentrate zinc toward the later stages of

differentiation. His findings confirm the early results of Brundin (1933); the contradictory evidence presented by Sandell and Goldich (1943) may be caused by regional differences in the zinc content. The content of zinc in some igneous rocks is presented in Table 38.1, according to the values given by Lundegårdh (1948).

Zinc and cadmium become strongly enriched in the hydrothermal rocks formed at relatively low temperatures. Nearly all known zinc minerals belong to such formations. The following list includes the

TABLE 38.1
CONTENT OF ZINC IN SOME IGNEOUS ROCKS

Swedish Rocks of the Ugranite Suite	Zn (g/ton)
Gabbro	90
Quartz diorite, diorite	120
Granodiorite, quartz syenite	200
Plagioclase granite	150
Plagioclase-microcline granite	30

most important species, with the exception of the two zincian spinels already mentioned:

Sphalerite and wurtzite,	ZnS
Zincite,	ZnO
Smithsonite,	ZnCO ₃
Willemite,	Zn ₂ [SiO ₄]
Hemimorphite,	Zn ₄ [(OH) ₂ Si ₂ O ₇]·H ₂ O

The simple metasilicates, ZnSiO₃ and CdSiO₃, are unknown. Sphalerite, with a theoretical zinc content of 67 per cent, is the most important ore mineral of zinc, but the other minerals listed above are also used as zinc ores, particularly when found in mineral veins.

Cadmium reveals its oxyphile character in igneous rocks less clearly than zinc does. The cadmium content of igneous rocks is several hundred times lower than that of zinc. Cadmium is much less abundant than zinc, and the abundance ratio of the two elements in igneous rocks is Zn: Cd ~ 900: 1. In spite of the similarity of the radii of Cd²⁺ (1.03 kX) and Ca²⁺ (1.06 kX), the former cannot enter the feldspar structure, as was proved by Schiebold (1931). Goldschmidt and Hörmann (Goldschmidt, 1937*b*) have found notable concentrations of cadmium (about 5 g/ton) in certain plagioclase rocks, but the manner of occurrence of cadmium in these rocks is still unknown, and actually cadmium very seldom becomes enriched in igneous rocks.

The information concerning the changes of cadmium content during magmatic differentiation is still controversial. Preuss (1941) re-

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ports an average content of 0.2 g/ton Cd in granites and less than 0.02 g/ton in gabbros, whereas the content given by Sandell and Goldich (1943) is 0.12 g/ton in granites and 0.2 g/ton in basic rocks.

Owing to its weaker oxyphile character, cadmium becomes nearly quantitatively enriched in hydrothermal rocks and minerals, and its highest concentrations are met in formations belonging to the lowermost temperatures. Greenockite, CdS, is found in low-intensity hydrothermal deposits. Zinc often appears already in perimagmatic mineral assemblages, e.g., in many contact rocks, whereas cadmium is most strongly enriched in ores with a more or less pronounced apomagmatic character.

According to Sandell and Goldich (1943), cadmium, like zinc, seems to be concentrated in ferromagnesian minerals. The major part of cadmium in acidic igneous rocks is present in biotite. Traces of cadmium have also been reported in apatite. Cadmium has a notable tendency to become concealed in the sphalerite structure, but other zinc minerals also regularly contain small quantities of cadmium. The most important zinc compound found in Nature, viz., zinc sulfide, is dimorphic, being found both as sphalerite and as wurtzite, which is the rarer and the more unstable of the two. The corresponding cadmium compound, greenockite, CdS, is one of the few independent cadmium minerals. It is frequently present as a thin coating on the surface of zinc minerals, especially on weathering sphalerites rich in cadmium. The structure of greenockite is analogous to that of wurtzite and thus differs from that of sphalerite. The radii of Zn^{2+} and Cd^{2+} differ notably from each other, and this circumstance is evidently responsible for the separation of cadmium sulfide as greenockite during the weathering of sphalerite. This is another example of the fact that two ions with considerably varying dimensions may replace each other diadochically at elevated temperatures, being, however, readily separated from each other at lower temperatures in two compounds. Another rare cadmium mineral, cadmium oxide, CdO, is found as a coating on hemimorphite.

CYCLE OF ZINC AND CADMIUM

Zinc goes readily into solution as sulfate or chloride during the weathering, and these compounds are transported in surface and ground waters. Zinc deposits may undergo enrichment in the zone of weathering, whereby zinc is redeposited as sulfide, oxide, carbonate, or silicate, and the process may lead to complete extraction of zinc

from the upper parts of zinc-ore bodies. The Zn^{2+} ion is consequently very mobile; according to Wickman (1944) it lies on the border between the soluble cations and the elements of hydrolyzates (see chap. 5). Cadmium is also dissolved as sulfate and chloride, but, because of its higher affinity for sulfur, it is precipitated as greenockite and becomes enriched in the zone of reduction. No cadmium is present in the resistates (Preuss, 1941). Zinc and cadmium, together with other elements having a high affinity for sulfur, are precipitated and enriched in hydrolyzates, especially in sulfur-bearing muds. The enrichment of zinc is often rather pronounced, if compared with its concentration in igneous rocks. The zinc content of sediments and sedimentary rocks is presented in Table 38.2, which is based on information given by Palmqvist (1935) and Lundegårdh (1948). The enrichment of cadmium is not very pronounced. Preuss (1941) reports an average content of 0.3 g/ton Cd in shales.

TABLE 38.2
ZINC CONTENT OF SEDIMENTS AND
SEDIMENTARY ROCKS

Material	Zn (g/ton)
Jotnian sandstone.....	<20
Clays ..	80-230
Shales	200-1,000
Oolite	80
Siderite.....	40
Ordovician limestone..	≧50

Although shales containing organic remains are often rich in zinc and cadmium, the highest concentration of these metals occurs in places where the production of hydrogen sulfide by decaying organisms has been rather weak. Thus, for example, the Mansfeld *Kupferschiefer* in Germany does not contain zinc and cadmium enriched in the same horizons as those in which copper is enriched. The two metals accompany lead and occur in zones independent of those of copper. Sphalerite is sometimes present in the Cambrian alum shales of Sweden (Lundegårdh, 1948).

The oxidate sediments, e.g., the manganese-rich lake and bog ores, adsorb significant amounts of zinc and cadmium. Zinc remains, in part, in sea water and is finally deposited in carbonate sediments. Smithsonite, the zinc carbonate, is isomorphic with calcite, as is also otavite, the cadmium carbonate, CdCO_3 . Otavite, as a coating on sphalerite and smithsonite, is a product of weathering, and its manner of occurrence is therefore similar to that of greenockite. Nothing

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is known, so far, of the occurrence of cadmium in carbonate sediments. Both zinc and cadmium, on the other hand, are considerably enriched in phosphorite deposits of organic origin. Brundin (1933) reports several thousand grams per ton of zinc in the sedimentary phosphates of the South Sea Islands. The content of cadmium in the phosphate rock may be as high as about 100 g/ton.

BIOGEOCHEMISTRY OF ZINC AND CADMIUM

Zinc is an essential element in the biosphere. In low concentrations it stimulates the growth of plants, but in large quantities it is very toxic to most plants. Sometimes it is concentrated by plants: a maximum of 16 per cent Zn is reported in the ashes of *Thlaspi calaminata*. Zinc is also enriched in coal ashes (chap. 8). In addition, it becomes fixed in soil, and in this process some micro-organisms seem to be of importance. In marine organisms the highest zinc content is found in oysters. Zinc is essential also for higher animals.

Cadmium has been found in some mollusks and annelids, but its significance in organisms is still unknown.

MERCURY

ABUNDANCE AND GEOCHEMICAL CHARACTER

NOTWITHSTANDING its position in the same group of the Periodic System with zinc and cadmium, mercury deviates rather strongly from these metals with reference to its geochemical character. The information concerning the abundance of mercury in meteorites is scarce: Noddack and Noddack (1931*a*, 1934) report 0.2 g/ton Hg in the troilite of the Cañon Diablo meteorite, and they estimate the average content of mercury in chondrites to be less than 0.01 g/ton. Therefore, it seems to be probable that mercury, like zinc and cadmium, is concentrated in the sulfide phase and is geochemically a chalcophile element. In the lithosphere mercury is classified among the sulfophile elements (chap. 5). Owing to its relatively high volatility, some mercury is always present in the atmosphere and thus shows a well-defined atmophile tendency.

Mercury is definitely absent in the solar atmosphere. Goldschmidt (1937*b*) suggests 0.5 g/ton as its abundance in igneous rocks. The value given by Saukov (1946) is 0.077 g/ton.

MERCURY IN IGNEOUS ROCKS; ORES OF MERCURY

Zinc and cadmium are present only in traces in the early-separated magmatic sulfides. The absence of mercury is still more pronounced, and the mercury content of such sulfides is practically nil. As a matter of fact, mercury is almost completely absent in the early crystallates of magmas, and in rocks belonging to the main stage of crystallization its content is also rather low. The mercury content of various igneous rocks is presented in Table 39.1. The values show that the content of mercury in igneous rocks is rather uniform.

Compared with the enrichment of zinc and cadmium in the mineral assemblages belonging to the lowermost temperature ranges of the hydrothermal stage of crystallization, that of mercury is still more pronounced. Such concentration of mercury takes place in geologi-

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cally young volcanic areas, particularly in connection with zones of tectonic movements, where hot springs in fracture zones may sometimes contain mercury as readily soluble double sulfides. Hydrothermal sulfides, formed at low temperatures, usually contain small amounts of mercury.

According to Saukov (1946), mercury, as the Hg^{2+} ion (radius 1.12 kX), may replace Ca^{2+} (radius 1.06 kX), although this diadochy is very limited. Another possibility is the $\text{Hg}^{+}\text{-Ba}^{2+}$ diadochy, which explains the presence of mercury, in concentrations up to 0.5 per cent Hg, in some barites.

Mercury is one of the most typical telemagmatic metals. The sulfosalts of arsenic and antimony, e.g., tetrahedrite with up to 17 per cent Hg, may sometimes contain considerable amounts of mercury,

TABLE 39.1
AVERAGE CONTENT OF MERCURY IN IGNEOUS ROCKS

Rock	Hg (g/ton)
Gabbro (Stock and Cucuel, 1934)	0.079
Gabbro (Preuss, 1941)	0.1
Basic effusives (Saukov, 1946)	0.09
Granite (Stock and Cucuel, 1934)	0.058
Granite (Preuss, 1941)	0.01
Acidic intrusives (Saukov, 1946)	0.064

which in such cases is recovered as a by-product during the metallurgical treatment of the ores. Livingstonite, $\text{HgS} \cdot 2\text{Sb}_2\text{S}_3$, is sometimes associated with other sulfosalts. Cinnabar, HgS , occurs as the main sulfide mineral in most mercury deposits; small amounts of native mercury, Hg, are found in many deposits; local concentrations of metacinnabar, HgS , are met in some cases. All other mercury minerals are rare. Pyrite and marcasite are commonly associated with cinnabar, and native sulfur is present in some deposits.

Mercury is also obtained from some gold veins which carry it partly as a telluride (coloradoite, HgTe), partly as a gold amalgam. Silver and palladium amalgams are also known in Nature, and the oxide HgO (montroydite), a number of selenides, halogenides, and oxychlorides occur as minerals. The Almadén district in Spain is typical of the occurrence of mercury: the mercury minerals were deposited in a porous sandstone from hot thermal solutions.

CYCLE OF MERCURY

The quantitative cycle of mercury is still known very inadequately. The volatility of mercury facilitates its migration, and in this re-

spect mercury differs from all other metals. Mercury may migrate either in the native state or as the soluble mercuric chloride, HgCl_2 . In the presence of oxidizing agents cinnabar is oxidized to sulfate. The mercury content of some sedimentary rocks is given in Table 39.2.

The hydrolyzate sediments form the proper surroundings for the enrichment of mercury. It is evident that the mercury content of

TABLE 39.2
CONTENT OF MERCURY IN SEDIMENTARY ROCKS

Rock	Hg (g/ton)
Sandstones, average (Preuss, 1941)	0.1
Sandstone (Stock and Cucuel, 1934)	0.033
Shales, average (Stock and Cucuel, 1934)	0.51
Shales, average (Preuss, 1941)	0.3
Chinle shale, average (Lausen, 1936)	40
Limestone (Stock and Cucuel, 1934)	0.033

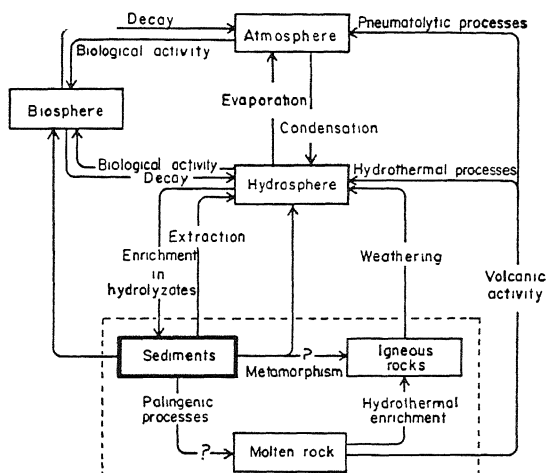


FIG. 39.1.—The cycle of mercury

shales is decidedly higher than that of igneous rocks. The enrichment of mercury in hydrolyzate sediments was explained by Goldschmidt (1937*b*), who assumed that, like boron, sulfur, and chlorine, mercury has also been largely introduced into the sea by volcanic emanations. Therefore, only a minor proportion is furnished by the weathering of rocks. The content of mercury is kept very low in sea water by its adsorption into the hydrolyzate and oxidate sediments.

The relatively high vapor pressure of mercury causes its presence in small amounts in the air, which are produced by its evaporation

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from the land surface. The mercury evaporated into the atmosphere returns in rain water. Stock and Cucuel (1934) found an average content of 0.002 g/ton Hg in rain water. The content in spring water is 0.0001–0.0005 g/ton and in sea water 0.0003 g/ton.

The cycle of mercury is presented in Figure 39.1.

MERCURY IN THE BIOSPHERE

Both plants and animals are able to concentrate mercury, but its physiological significance, if any, is still unknown. Marine algae may concentrate mercury, and some species are found which contain more than a hundred times as much mercury as sea water does. In exceptional cases mercury is concentrated as native mercury in some land plants. Vegetable fats are relatively rich in mercury. All fishes are also rich in mercury; Stock and Cucuel (1934) report a maximum content of 0.18 g/ton. In higher vertebrates mercury concentrates in the kidney. Fossil coals are not rich in mercury, but in this case the vapor pressure of the metal might be instrumental in decreasing its concentration. In view of the toxic effect of mercury, the depoisoning of sea water by precipitation in the hydrolyzates is of high importance for the presence and development of higher forms of life in the oceans.

GALLIUM, INDIUM, THALLIUM

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE abundance of gallium, indium, and thallium in the meteorite phases and in igneous rocks is, so far, somewhat incompletely known. The values thought to be the most reliable are recorded in Table 40.1. The values are presented according to the following authorities: all gallium values, indium in nickel-iron, troilite, and igneous rocks, and the lower limit of thallium in igneous rocks from Goldschmidt (1937*b*); indium and thallium in the silicate phase of

TABLE 40.1
ABUNDANCE OF GALLIUM, INDIUM, AND THALLIUM

MATERIAL	Ga	In	Tl
	g./ton		
Nickel-iron of meteorites	8	0.5	unknown
Troilite	8	0.5	0.3
Silicate phase of meteorites	3	0.24	0.15
Igneous rocks	15	0.1	0.3-3

the meteorites from Noddack and Noddack (1934); thallium in troilite from Noddack and Noddack (1930); the upper limit of thallium in igneous rocks from Ahrens (1947*b*). The values found for igneous rocks are probably relatively accurate, but the other values are still only tentative. It may be added that van Tongeren (1938) reported the average of 42 g/ton Ga for igneous rocks of the Dutch East Indies. The high gallium content may be a regional peculiarity of this area. The value given by Ahrens (1947*b*) for thallium, viz., 3 g/ton, is based on the observed close association of thallium and rubidium in minerals and on the assumption that in the upper lithosphere the ratio Rb:Tl is about 100:1. Ahrens' value does not agree with the rule of Oddo and Harkins. Being derived largely from anal-

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yses of potassium minerals of acidic igneous rocks, this value is undoubtedly too high.

At any rate, the values recorded in Table 40.1 show that all the three metals are conspicuously chalcophile in physicochemical systems containing a sulfide phase. Gallium is, in addition, siderophile, even though its character is not pronouncedly so. Furthermore, all these elements possess lithophile tendencies, gallium being the most pronouncedly lithophile of the three. The lithophile character of indium is rather weak. This discussion shows that the general geochemical character of these metals is rather versatile. Both their chalcophile and their lithophile properties determine their manner of occurrence in the lithosphere.

The abundance of gallium and indium in the solar atmosphere is known, but thallium is absent therein.

MANNER OF OCCURRENCE IN IGNEOUS ROCKS; ORES

In the geochemical classification of the elements presented by Vernadsky (1924), both gallium and indium were included in the group of the typically dispersed elements. According to Vernadsky, the two elements are nowhere enriched; they are of widespread occurrence but always in very small concentrations. Consequently, Vernadsky considered gallium and indium very scarce elements. So far, no minerals have been found which contain these metals as essential constituents. However, it is known that gallium and indium may become enriched in certain minerals and rocks. It should also be noted that the abundance estimated for gallium by Vernadsky is too low. This circumstance was actually discovered, long before Vernadsky's studies, by Hartley and Ramage (1897), who were able to show that numerous minerals, rocks, and ores, particularly magnetite, contain considerable quantities of gallium. Consequently, gallium is not among the least abundant of the elements. In their studies Hartley and Ramage also recorded the widespread occurrence of indium and thallium in minerals and rocks.

In the upper lithosphere gallium, indium, and thallium are rather strongly oxyphile (chap. 5). The greatest part of all gallium present in the upper lithosphere is met in silicate minerals, in which its manner of occurrence is governed by the diadochy between the trivalent ions Ga^{3+} and Al^{3+} . The radii of the two ions are very nearly equal, viz., 0.62 and 0.57 kX, respectively. Therefore, gallium encounters no difficulties in replacing aluminum diadochically in 6-co-ordina-

tion. It is, in addition, able to form $[\text{GaO}_4]$ tetrahedra, which may replace the $[\text{AlO}_4]$ tetrahedra in certain silicates.

Wickman (1943) explained the camouflage of gallium by aluminum. The reason is that the E -values of the two metals are similar and that aluminum, an abundant element, takes an active part in the formation of minerals. The E -value of 4-co-ordinated gallium must be lower than that of aluminum because gallium becomes enriched during the differentiation. Because the charge of the surrounding anions influences the E -values of cations, the gallium ions, when co-ordinated with fluorine, migrate readily, and the result is a low gallium content of aluminum fluoride minerals. On the other hand, gallium becomes stabilized when co-ordinated with oxygen ions and consequently enters silicate minerals.

The concealing of gallium in minerals in the place of aluminum is by far its most important manner of occurrence in minerals, with the exception of sulfides. The similarity of the radii of Ga^{3+} , Cr^{3+} (0.64 kX), and Fe^{3+} (0.67 kX) is responsible for the presence of gallium in some chromites and early magmatic iron ores (Einecke, 1937); Goldschmidt and Peters (1931a) report up to about 7 g/ton Ga in early-separated chromites, magnetites, and sulfide minerals. Thus, as emphasized by Wickman (1943), the earliest products of differentiation already show Ga:Al ratios not materially different from those found in minerals crystallizing from the residual solutions. Among the aluminum minerals, practically only the pneumatolytic fluoride cryolite, $\text{Na}_3[\text{AlF}_6]$, is devoid of gallium. Goldschmidt and Peters (1931a) report much less than 3.7 g/ton Ga in cryolite from Ivigtut, Greenland; sphalerite from the same locality contains nearly 74 g/ton Ga. Gallium is known to become concentrated, along with aluminum, in pegmatites, notably in those approaching hydrothermal characteristics. However, the values cited above show that, when the deposition of sulfides begins, gallium deserts aluminum in favor of sphalerite (Graton and Harcourt, 1935).

Even though gallium closely accompanies aluminum in rocks, the geochemical coherence of the two metals is rather weak, and their abundance ratio does not remain constant, as was shown by Goldschmidt and Peters (1931a). As has been repeatedly mentioned, gallium is somewhat enriched in the late crystallates during the magmatic differentiation. This behavior is also shown by the regional studies of van Tongeren (1938) and Sahama (1945b). Greisen is especially high in gallium (Goldschmidt, Hauptmann, and Peters,

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1933). The changes in the Ga:Al ratio in minerals crystallized during the various stages of differentiation are shown in Table 40.2, based on values reported by Goldschmidt and Peters (1931*a*). It is evident that even small differences in ionic radii make possible the enrichment of the larger component in late crystallates and in mother-liquors. The values in Table 40.2 show, in addition, that the Ga:Al ratio varies from about 1:10 to about 1:100,000, or by more than 10^4 . In the pair hafnium-zirconium, the Hf:Zr ratio never varies more than by $5 \cdot 10^2$ (see chap. 21), and consequently the camouflage in this pair is much more complete than in the pair gallium-aluminum. The ionic radii of the elements in question and the basicity of their hydroxides make this result obvious.

TABLE 40.2
CHANGES IN GALLIUM CONTENT AND IN THE Ga:Al RATIO
DURING MAGMATIC DIFFERENTIATION

Material	Ga (g/ton)	Ga:Al
Bytownite, Sogndal, Norway	3.7	1:120,000
Nepheline, Langesundsfjord, Norway	74	1:6,000
Diaspore, Langesundsfjord, Norway	1,480	1:800
Opalized wood, Yellowstone National Park, Wyoming, U.S.A.	740	1:13

The aluminum minerals of pegmatites, in particular, e.g., muscovite, lepidolite, and tourmaline, are considerably enriched in gallium. Goldschmidt and Peters (1931*a*) found in excess of 70 g/ton Ga in a muscovite.

With reference to the hydrogen-ion concentration, the precipitation intervals of $\text{Ga}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ differ distinctly, even though not pronouncedly, from each other. Because gallium hydroxide is somewhat less basic than aluminum hydroxide, gallium becomes strongly enriched in hot alkaline aqueous solutions with respect to aluminum. It is consequently often found in notable concentrations in sediments deposited from thermal waters, e.g., in siliceous sinters (see Table 40.2), whereas its content in low-temperature hydrothermal chalcedony and opal is negligible. The gallium content of zeolites shows that when the late hydrothermal stage in crystallization has been reached, only minute amounts of gallium will be deposited in the zeolites of the normal calc-alkalic rocks, whereas the zeolites in the alkalic rocks rich in aluminum may run high in gallium (cf. diaspore in Table 40.2).

The manner of occurrence of indium in igneous rocks is notably different from that of gallium. Indium has a fair tendency to combine with sulfur, and therefore it is less completely bound within silicate structures. The radius of the In^{3+} ion is 0.92 kX, or considerably greater than that of Ga^{3+} ; and this fact evidently explains the capturing of the In^{3+} ions by Fe^{2+} , with a radius of 0.83 kX, and by Mn^{2+} (radius 0.91 kX). This type of replacement is sometimes met in minerals. Such is the case in the common enrichment of indium in pyroxeniferous basic rocks, which was established by Goldschmidt and Hörmann (Goldschmidt, 1937*b*). No indium is usually present in dunites and gabbros (Borovick, Prokopenko, and Pokrovskaya, 1939), although it may sometimes occur in traces in the early-separated sulfides (pyrrhotite). According to Prokopenko (1941), indium is concentrated mainly in sulfides associated with granites, granodiorites, and monzonites. Although some indium is confined to intermediate, acidic, and alkalic rocks, most of it remains in the residual melt throughout the main stage of magmatic crystallization and sometimes is subsequently notably enriched in the dark constituents of pegmatites, such as columbite, $(\text{Fe,Mn})(\text{Cb,Ta})_2\text{O}_6$. The presence of indium in cassiterite was noticed years ago by Hartley and Ramage (1897), who also detected its constant occurrence in siderite. Ottemann (1941) reported the presence of indium in tin-rich silicate minerals connected with pneumatolytic processes producing cassiterite, e.g., in biotite and tourmaline. In cassiterite, on the other hand, the content of indium is low (Erämetsä, 1938). Goldschmidt (1937*b*) found about 0.5 g/ton In in muscovite, and Romeyn (1933) reported 1.0–2.8 per cent In in a pegmatite from Utah, in the United States; his observation has not been confirmed.

In its manner of occurrence in igneous rocks thallium differs very sharply from the other two metals in question. In spite of its rather strong affinity for sulfur and selenium, thallium is also a definite constituent of many silicate minerals. These minerals contain thallium in the form of Tl^+ ions with a radius of 1.49 kX, or equal to that of Rb^+ . The Tl^+ ion is therefore able to replace K^+ in potash feldspars; in the plagioclase feldspars, according to Ottemann (1941), Tl^{3+} (radius 1.05 kX) may be captured by Ca^{2+} (radius 1.06 kX); the content in plagioclase may be as high as 10 g/ton. The artificial soluble inorganic thallos compounds and the corresponding rubidium compounds are usually isomorphic, and the soluble compounds of univalent thallium resemble those of the alkali metals chemically in

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many respects. In igneous rocks univalent thallium often accompanies rubidium and is concentrated with it. In potassium minerals like leucite, the potash feldspars of the pegmatites, and muscovite the thallium content along with that of rubidium may sometimes be very considerable. Goldschmidt and Hörmann (Goldschmidt, 1937*b*) found up to 20 g/ton Tl in leucite and nearly 100 g/ton in amazonite. Ahrens (1947*a*) reported a notable enrichment of thallium in pollucite. He found (Ahrens, 1945) in lepidolites and muscovites from granites and granite pegmatites a maximum of 221 g/ton and 58 g/ton Tl, respectively. Furthermore, Ahrens (1948*a*) emphasized the close association of thallium and rubidium in minerals formed during the latest stages of magmatic crystallization, because he was unable to detect any changes in the Rb:Tl ratio during these stages.

In the minerals of pneumatolytic tin-bearing rocks, thallium is enriched still more strongly than is indium. Ottemann (1941) found up to 100 g/ton Tl in biotites from pneumatolytic rocks from the Harz Mountains in Germany. Thallium was present also in plagioclase (see above), tourmaline, diallage, and quartz.

It must be mentioned, with reference to the occurrence of thallium in feldspars, that the alkali metals and thallium, according to Schiebold (1931), are the only univalent metals capable of forming a feldspar structure (see chap. 5).

The most typical feature of the geochemistry of univalent thallium in igneous rocks is its strong concentration in pegmatites. Also in this respect it closely resembles rubidium. The two metals are typical of the late crystallates.

With the exception of gallium, abundance determinations of the three metals in igneous rocks are too few. The most reliable values, obtained from a number of sources, are presented in Table 40.3. The values reported confirm the geochemical behavior of the three metals as discussed above.

In accordance with their strong affinity for sulfur, all three metals are found in sulfide minerals and other comparable minerals. Usually they are not notably concentrated in the early-separated sulfides but are found, together with a host of other chalcophile elements, in products of pneumatolytic and hydrothermal activity. The sphalerite structure, in particular, is an important habitat of both gallium and indium. According to Oftedal (1940), only sphalerite among the common sulfide minerals is gallium-bearing. No independent gallium and indium minerals are known. The two metals are recovered as by-

GALLIUM, INDIUM, THALLIUM

products of the metallurgical treatment of sphalerite ores. According to Goldschmidt and Peters (1931*a*), gallium is concealed in sphalerite as the arsenide, GaAs, because the crystal structure and structural dimensions of the two compounds are nearly equal. However, Graton and Harcourt (1935) emphasized the fact that evidence concerning the arsenic content of galliferous sphalerites is still insufficient to

TABLE 40.3

ABUNDANCE OF GALLIUM, INDIUM, AND THALLIUM IN IGNEOUS ROCKS

Material	Ga (g/ton)
Dunites (Goldschmidt and Peters, 1931 <i>a</i>) . . .	≪ 3.7
Eclogites (Goldschmidt, 1937 <i>c</i>)	7 4
Gabbros (Goldschmidt, 1937 <i>c</i>)	7 4
Granites (Goldschmidt, 1937 <i>c</i>)	14 8
Nepheline syenites (Goldschmidt, 1937 <i>c</i>)	14.8
Greisen (Goldschmidt, Hauptmann, and Peters, 1933) . .	74
Pegmatite minerals (Goldschmidt, 1937 <i>c</i>)	up to 74
Intermediary igneous rocks, average (Sandell, 1947) . . .	14 5
Basic igneous rocks, average (Sandell, 1947)	12 75
Gabbros and dolerites of southern Lapland, average (Sahama, 1945 <i>b</i>)	22
Granites of southern Lapland, average (Sahama, 1945 <i>b</i>) .	74
Syenites of southern Lapland, average (Sahama, 1945 <i>b</i>) .	74

Material	In (g/ton)
Pyroxeniferous basic igneous rocks, average (Goldschmidt and Hörmann in Goldschmidt, 1937 <i>b</i>)	0.5-1
German gabbros, average (Preuss, 1941)	0 3
German granites, average (Preuss, 1941)	2

Material	Tl (g/ton)
German gabbros, average (Preuss, 1941)	0 3
Granites and liparites (Goldschmidt and Hörmann in Goldschmidt, 1937 <i>b</i>)	0.5-1
German granites, average (Preuss, 1941)	3
Granites of the Harz Mountains, Germany (Ottemann, 1941)	1.5

show the validity of this suggestion. Einecke (1937) found the presence of gallium phosphide, GaP, in sphalerite possible because of structural reasons. He considered, in addition, the possibility of the replacement of Zn^{2+} by Ga^{2+} in the sphalerite structure as another explanation of the gallium content of sphalerite.

Indium, according to Erämetsä (1938), is captured in the sphalerite structure as In^{3+} ions (radius 0.92 kX), which are rather similar to Zn^{2+} ions (radius 0.83 kX) in their dimensions. Erämetsä showed that sphalerite is a very sensitive indicator of indium and often collects all available indium during its crystallization. According to

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Erämettä the content of indium in sphalerite shows pronounced regional variations. This is due to the fact that, contrary to the opinion expressed by Vernadsky (1924), indium is not an omnipresent element but is concentrated, more or less, in certain geological formations in which it is encountered in sphalerite ores. According to Erämettä, the sphalerites of Pitkäranta and some other localities in eastern Fennoscandia contain considerable amounts of indium (up to 1 per cent), whereas the content in some other sphalerites is low. In the indium-rich areas (indium provinces) silicate minerals, e.g., amphiboles, may also be indium-bearing. With reference to the occurrence of gallium and indium in sphalerite, it must be noticed, in addition, that indium is often most abundant in sphalerites crystallized at intermediate temperatures, whereas the content of gallium is at its highest in the low-temperature minerals, although this rule may not be generally valid (Ofstedal, 1940). Sphalerite is the most important ore mineral of indium, but many other sulfides also contain notable quantities of this metal, e.g., chalcopyrite (Hartley and Ramage, 1897; Erämettä, 1938) and many pneumatolytic tin and tungsten minerals of granitic rocks (Hartley and Ramage, 1897). Goldschmidt and Hörmann (Goldschmidt, 1937b) found 0.5–10 g/ton In in stannite, cassiterite, wolframite, and triplite. In these minerals In^{2+} replaces partly Fe^{2+} and partly Sn^{4+} (radius 0.74 kX). Among the sulfide minerals the highest content of gallium is found in germanite, $\text{Cu}_2(\text{Fe}, \text{Ge})\text{S}_4$, which has a maximum of 1.85 per cent Ga.

The manner of occurrence of thallium in sulfide minerals differs notably from that of the other two metals discussed. In silicate minerals, lead partially adopts the manner of occurrence of thallium and rubidium, e.g., in potash feldspars. A similar geochemical alliance between lead and thallium characterizes their occurrence in sulfide minerals. Among the three metals discussed in this chapter, only thallium forms independent minerals. It seems that thallium, of the three metals, becomes most prominently enriched in certain rocks. This property of thallium is displayed already by the way it occurs in igneous rocks, in which it is concentrated into pegmatites. The independent thallium minerals are lorandite, $\text{Tl}_2\text{S} \cdot \text{As}_2\text{S}_3$ (about 60 per cent Tl); crookesite, $\text{Cu}_{13}\text{Tl}_2\text{AgSe}_3$; vrbaite, $\text{Tl}_2\text{S} \cdot 2\text{As}_2\text{S}_3 \cdot \text{Sb}_2\text{S}_3$; and hutchinsonite, $\text{PbS} \cdot (\text{Ag}, \text{Tl})_2\text{S} \cdot 2\text{As}_2\text{S}_3$, which, however, are very rare. The most important hosts of thallium among sulfide minerals are galena, in which it replaces lead, and various sulfosalts, particularly

those containing lead, such as sartorite, $PbS \cdot As_2S_3$; dufrenoy-site, $2PbS \cdot As_2S_3$; and jordanite, $4PbS \cdot As_2S_3$. Thallium is recovered as a by-product of metallurgical processes using ores containing these minerals. Oftedal (1940) found thallium only in galena; the other common sulfide minerals were devoid of this metal. The often reported occurrence of thallium in pyrite is probably erroneous Goldschmidt, according to Oftedal, 1940).

GEOCHEMICAL CYCLES

During weathering, gallium follows aluminum rather closely and is deposited from the resulting solution into the hydrolyzates, together with its host metal. It is therefore an element typical of the hydrolyzates. Bauxites are especially rich in gallium. Small amounts of gallium may also be present in the oxidates, owing to the replacement of Fe^{3+} by Ga^{3+} referred to above. Such is the explanation of the gallium content of the red clay. The marine carbonate sediments are low in gallium. According to Goldschmidt and Peters (1931a), the Ga:Fe ratio in sedimentary iron ores is of the order of 1:100,000 or 1:200,000, whereas the average Ga:Al ratio in argillaceous sediments is about 1:30,000. These values show that gallium does not accompany iron during the exogenic cycle but follows aluminum at close quarters. The difference in the normal potentials of gallium and aluminum does not suffice to separate the two metals from each other in the exogenic cycle without the action of sulfides and arsenides.

Papish and Stilson (1930) found no gallium in the oxidation products of sphalerite, e.g., in smithsonite, whereas cadmium is known to be present therein. Gallium is therefore removed in solution during the weathering of sphalerite. There is, consequently, a pronounced difference between the cycles of gallium and cadmium, which are common minor constituents of sphalerite.

Indium is deposited in the oxidates, in which it once more replaces Fe^{2+} and Mn^{2+} . It is also present in sedimentary siderites and in iron sulfides of sedimentary origin. Likewise, indium is concentrated in marine phosphates (Goldschmidt, 1937a). Borovick, Prokopenko, and Pokrovskaya (1939) found indium in clays only in individual cases, the maximum content being 10 g/ton In. They were unable to find indium in marine muds. Indium borate, $InBO_3$, is isomorphic with calcite, $CaCO_3$ (Goldschmidt and Hauptmann, 1932), and may consequently be present in marine carbonates.

The cycle of thallium is known very inadequately. Owing to the

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low solubility of thallous chloride, $TlCl$, it is probable that thallium is largely precipitated already in hydrolyzate sediments. Some thallium is present in sea water, being finally deposited in marine evaporates. Thallium has been found in sylvite and carnallite. Many mineral waters contain thallium (as well as gallium), which is apparently of juvenile origin.

The content of gallium, indium, and thallium in some sediments and sedimentary rocks is recorded in Table 40.4. The number of analyses is still far from satisfactory.

TABLE 40.4
CONTENT OF GALLIUM, INDIUM, AND THALLIUM IN
SEDIMENTS AND SEDIMENTARY ROCKS

Material	Ga (g/ton)
Sandstones, average (Goldschmidt and Peters, 1931a)	7.4
Kaolin, average (Goldschmidt and Peters, 1931a)	7.4
Bauxite, average (Goldschmidt and Peters, 1931a) . . .	22.2
Russian clays, composite sample (Borovick, Prokopenko, and Pokrovskaya, 1939)	50
Sedimentary iron and manganese ores (Goldschmidt and Peters, 1931a)	usually 3.7 or below
Mesozoic limestones, average (Goldschmidt and Peters, 1931a)	3.7 or below
Material	In (g/ton)
German sandstones, average (Preuss, 1941)	0.3
German shales, average (Preuss, 1941)	0.5
Material	Tl (g/ton)
German sandstones, average (Preuss, 1941)	2
German shales, average (Preuss, 1941)	2

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Probably, gallium is an element essential to the fungus *Aspergillus niger*, and it may have importance also for higher plants. Mitchell (1944) reports 5–300 g/ton Ga in soil. Gallium is enriched in coal ashes (Goldschmidt and Peters, 1933c). Haberlandt (1944) found gallium as a major constituent in a porphyrin complex isolated from a hydrothermal calcite, and he suggests that gallium was probably taken up by organic substances from gallium-bearing thermal waters. Gallium is also reported as a constituent of marine organisms.

No information is available on the occurrence of indium in organisms. Nothing is known about its concentration in coal ashes.

Thallium is present in plants as a rather common constituent, but information concerning its concentration in coal ashes is still lacking. It is concentrated by certain marine animals.

GERMANIUM, TIN, LEAD

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

GERMANIUM and lead have been quantitatively determined in the solar atmosphere, and tin is probably also present therein. The abundance of the three metals has been determined by Goldschmidt and Peters (1933*a*, germanium; 1933*b*, tin), Goldschmidt (1937*b*, tin, lead), Noddack and Noddack (1930, 1931*a*, lead), and Hevesy (1932, lead). The most reliable values are given in Table 41.1. As the average for igneous rocks of Dutch East Indies van Tongeren (1938) obtained 23 g./ton Pb.

TABLE 41.1
ABUNDANCE OF GERMANIUM, TIN, AND LEAD IN
METEORITES AND IN IGNEOUS ROCKS

MATERIAL	Ge	Sn	Pb
	g/ton		
Nickel-iron.	500	100	56
Troilite.	30	15	20
Silicate meteorites	5	5	2
Igneous rocks	4	40	16

The values recorded in Table 41.1 show that germanium and tin are very pronouncedly siderophile, and it is evident that they are concentrated in the nickel-iron core of the Earth. The troilite values show that germanium is also chalcophile; but in highly reducing surroundings and at elevated temperatures, as in the parent-planet of the meteorites, its siderophile properties predominate. Lead seems to be chiefly siderophile, but its relative content in troilites is somewhat higher than that of the other two metals, and hence it should also be chalcophile. Because the abundance values given for lead are not final, it might be possible that the lead content of troilite is somewhat higher than indicated. In the lithosphere lead shows a rather pro-

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nounced affinity for sulfur and also for oxygen; in igneous rocks tin predominates over the other two metals discussed in this chapter.

OCCURRENCE IN THE UPPER LITHOSPHERE; ORES

The manner of occurrence of germanium in the upper lithosphere greatly resembles that of gallium. The two metals are present both in sulfide and in silicate minerals. Germanium was previously considered an extremely rare element, and Vernadsky (1924) classified it among the typically dispersed elements. However, Papish (1929) showed that it is commonly met in a number of silicate minerals, especially in topaz, although usually only in small quantities. Gallium is camouflaged in silicates in the place of aluminum, and, according to Goldschmidt (1931b), in a similar way germanium diadochically replaces silicon and forms $[\text{GeO}_4]$ tetrahedra. The ionic radii of the two elements are alike ($r_{\text{Ge}^{4+}} = 0.44 \text{ kX}$; $r_{\text{Si}^{4+}} = 0.39 \text{ kX}$), and the germanates are usually isomorphic with the corresponding silicates. The structural relationships between GeO_2 , quartz, and rutile explain the presence of germanium in such titanium and tin minerals as ilmenite and cassiterite. Wickman (1943) stated that, on the whole, Ge^{4+} preferably substitutes Si^{4+} in the least-linked silicate tetrahedra. Therefore, topaz and garnet contain more germanium (up to 0.1 per cent Ge in topaz and spessartite, according to Oftedal, 1939a) than quartz, and hypersthene more than plagioclase. The E -values of silicon and germanium are so large that these elements always participate in mineral formation, but the binding energy of germanium is smaller than that of silicon (see chap. 5). The replacement of Si^{4+} by Ge^{4+} is the most conspicuous feature of the geochemistry of germanium, and most of germanium in the upper lithosphere is camouflaged in quartz and silicates: it is an oxyphile element (see chap. 5).

The content of germanium in igneous rocks is presented in Table 41.2. The values show that during magmatic differentiation germanium, in analogy with gallium, is somewhat concentrated in the later crystallates. The granites are high in germanium, whereas the content is a little lower in nepheline syenites. This rule is valid also for the pegmatites connected with these rocks. Only very little germanium is found in the early magmatic oxides, in which it follows titanium. Rocks and minerals connected with pneumatolytic processes are the highest in germanium, and it is strongly concentrated in greisen and its minerals. The residual solutions may deliver germanium directly to the exogenic cycle.

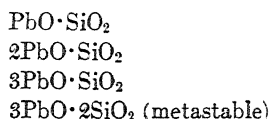
Furthermore, germanium is enriched in the siliceous sinters deposited from thermal waters and in the deposits of hot springs rich in iron and manganese. On the other hand, it is absent in silica and quartz formed at low temperatures but may be present in hydrothermal silicates.

With reference to their manner of occurrence, tin and lead in igneous rocks differ completely from germanium and also from each other. Tin and lead are both bivalent and quadrivalent. Tin does not seem to be able to crystallize from artificial SnO-SiO_2 and $\text{SnO}_2\text{-SiO}_2$

TABLE 41.2
AVERAGE CONTENT OF GERMANIUM IN IGNEOUS ROCKS

Rock	Ge g. ton.
Basic plagioclase rocks (Goldschmidt and Peters, 1933a)	2.1
Gabbros (Preuss, 1941)	2
Granites (Goldschmidt and Peters, 1933a)	3.5
Granites (Preuss, 1941)	3
Nepheline syenites (Goldschmidt and Peters, 1933a)	2.1
Greisen (Goldschmidt and Peters, 1933a)	35

melts as simple silicates, whereas lead is known to form the following compounds:



The last-mentioned compound occurs as the rare barysilite, $\text{Pb}_3[\text{Si}_2\text{O}_7]$, which is structurally analogous to thortveitite and contains independent $[\text{Si}_2\text{O}_7]$ groups. Lead shows a tendency to form numerous sulfides, selenides, sulfosalts, phosphates, arsenates, and silicates, many of which are chemically rather complicated. Native lead, Pb, is a mineralogical curiosity. According to Goldschmidt (1937b), a very considerable part of lead in igneous rocks occurs as galena. However, the calculations presented in chapter 5 show that in the upper lithosphere lead is an oxyphile element. With the exception of galena, the other lead minerals are usually without much geochemical moment. Compared with lead minerals, the independent tin minerals are less numerous. A number of oxide minerals of lead are known: the monoxide, PbO, occurs as massicot and litharge; the dioxide, PbO_2 , is found as plattnerite; and the oxide, Pb_3O_4 , minium, is known as an alteration product of galena and cerussite. All these minerals are rare. Tin monoxide, SnO, is not known as mineral, whereas the dioxide,

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SnO_2 , as cassiterite, is the most common of all tin minerals. It is evident that there is a certain analogy between the two metals and titanium and zirconium, which occupy adjacent positions in the Periodic Table. Titanium has a lower atomic number than zirconium, and its dioxide, TiO_2 , is rather common as a mineral, notably as rutile. Baddeleyite, ZrO_2 , the corresponding oxide of zirconium, the element with the higher atomic number, is rare.

In the upper lithosphere tin is oxyphile. It is rather strongly enriched in the late crystallates during magmatic differentiation. The tin content of igneous rocks is presented in Table 41.3. The values show that tin is typically met in granites. The highest content is found in pneumatolytic rocks, e.g., greisen.

TABLE 41.3
CONTENT OF TIN IN IGNEOUS ROCKS

Rock	Sn (g/ton)
Dunite (Goldschmidt and Peters, 1933b)	0
Plateau basalt (Goldschmidt and Peters, 1933b) .	4
Gabbro, average (Goldschmidt and Peters, 1933b)	8
Granite, average (Goldschmidt and Peters, 1933b)	80
Granite, average (Ottemann, 1941)	56
Nepheline syenite, average (Goldschmidt and Peters, 1933b)	8-40
Greisen, average (Goldschmidt and Peters, 1933b)	800-8,000

In silicate rocks tin is found as cassiterite and replacing a number of elements in silicate structures. The Sn^{4+} ion may replace Fe^{2+} , and Sn^{2+} substitute for Ca^{2+} . In some pegmatite minerals, Sn^{4+} may replace Sc^{3+} and Ti^{4+} . This explains the presence of tin in titanium minerals, for example, in sphene, which, according to Ramdohr (1936), may contain around 10 per cent tin, in columbates, in tantalates, and in thortveitite. In addition, quadripesitive tin may replace quinquepositive columbium and tantalum and quadripesitive tungsten, e.g., in wolframite, which may contain 1 per cent Sn (Ottemann, 1941). Ottemann has also found up to 300 g/ton Sn in biotites of pneumatolytic rocks. Other minerals of pneumatolytic parageneses may also carry tin, for instance, tourmaline, plagioclase (both up to 50 g/ton Sn), and fluorite. The general rule is that the content of tin in minerals increases parallel to their fluorine content; this should be due to the introduction of tin as the volatile tetrafluoride, SnF_4 . According to Ottemann, tin is able to enter silicate structures only to a limited degree, the excess being separated out as cassiterite.

The manner of occurrence of lead in igneous rocks is determined by a diadochic replacement similar to that valid for strontium. Lead is present in silicate and phosphate minerals as Pb^{2+} ions, with a radius of 1.32 kX. Like Sr^{2+} (radius 1.27 kX), lead partially replaces Ca^{2+} (radius 1.06 kX) diadochically and is found particularly in such calcium minerals as apatite (up to 50 g/ton Pb; Goldschmidt, 1937*b*) and the monoclinic pyroxenes, which have crystallized at a relatively high temperature. However, Pb^{2+} may also replace Ca^{2+} in minerals formed at lower temperatures. Aragonite may contain up to 18 per cent PbCO_3 (tarnowitzite). Ottemann (1941) reports 100 g/ton Pb in epidote, up to 77 g/ton in biotite, and 50 g/ton in fluorite. Lead is also present in potassium minerals, particularly in potash feldspars,

TABLE 41.4
LEAD CONTENT OF IGNEOUS ROCKS

Rock	Pb (g/ton)
Gabbros and related rocks, average (Hevesy, Hobbie, and Holmes, 1931)	5
Basic igneous rocks, average (Sandell and Goldich, 1943)	9
Granitic rocks, average (Hevesy, Hobbie, and Holmes, 1931)	30
Granites of southern Lapland, average (Sahama, 1945 <i>b</i>)	9-27
Acidic igneous rocks, average (Sandell and Goldich, 1943)	19

in which it diadochically replaces potassium (K^+ , radius, 1.33 kX), being captured in its place in the structure, like thallium. Therefore, the potash feldspars, e.g., in pegmatites, are often plumbiferous. Schiebold (1931) proved that lead is able to form a feldspar structure; a stable artificial lead feldspar has actually been prepared (chap. 5).

The content of lead in igneous rocks is presented in Table 41.4. The values show that lead, like tin, is rather strongly enriched in acidic igneous rocks.

The three metals discussed in this chapter are strangers among the early magmatic sulfides, being enriched particularly in pneumatolytic and hydrothermal formations. At low temperatures their affinity for sulfur is clear enough, whereas in minerals formed at intermediate and high temperatures they occur almost exclusively as oxygen-bearing compounds. Under pneumatolytic and hydrothermal conditions germanium is a common constituent of sphalerite and other sulfides and sulfosalts, which contain it usually in the company of tin. It is enriched in minerals formed at low temperatures. In arsenides, sulf-

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arsenides, and antimonides the content of germanium is negligible. Germanium forms the rare minerals argyrodite, $4\text{Ag}_2\text{S} \cdot \text{GeS}_2$ (with 5–7 per cent Ge); germanite, $\text{Cu}_3(\text{Fe}, \text{Ge})\text{S}_4$ (up to 10 per cent Ge); and ultrabasite, $28(\text{Pb}, \text{Fe})\text{S} \cdot 11(\text{Ag}, \text{Cu})_2\text{S} \cdot 3\text{GeS}_2 \cdot \text{Sb}_2\text{S}_3$. In the sulfosalts germanium usually forms a negatively charged complex GeS_n^- .

Along with cassiterite the following sulfosalts of tin are of some importance, all of which are found as constituents of tin ores:

Stannite,	$\text{Cu}_2\text{FeSnS}_4$
Kylindrite,	$6\text{PbS} \cdot 6\text{SnS}_2 \cdot \text{Sb}_2\text{S}_3$ (?)
Teallite,	PbSnS_2

Other sulfide minerals containing tin are sphalerite, galena, and chalcopyrite. Pyrite and pyrrhotite are free of tin (Oftedal, 1939*a*). Goldschmidt (according to Oftedal, 1939*a*) explained this manner of occurrence by the structural relationships between stannite and the three first-mentioned sulfides. Tin is also met as a constituent of certain rare borates and silicates. However, the economically most important mineral of tin is cassiterite.

The most important lead minerals include the following species:

Galena,	PbS
Cerussite,	PbCO_3
Anglesite,	$\text{Pb}[\text{SO}_4]$
Pyromorphite,	$\text{Pb}_5[\text{Cl}](\text{PO}_4)_3$

These minerals and the various sulfosalts of lead are the most notable constituents of lead deposits, galena with 86.5 per cent Pb being the most prominent of all. In addition, it is the most important silver mineral (up to 2 per cent Ag). Cerussite, anglesite, pyromorphite, and many other sulfate, carbonate, and chloride minerals of lead are usually found as alteration products of galena in the superficial parts of lead-ore bodies. The chromate crocoite, $\text{Pb}[\text{CrO}_4]$, and the molybdate wulfenite, $\text{Pb}[\text{MoO}_4]$, are also of secondary origin. The occurrence of lead in certain radioactive minerals as the stable product of disintegration deserves special mention.

Contrary to galena, the corresponding tin monosulfide SnS , herzenbergite, is very rare and consequently without geochemical importance.

Many lead and tin ores are genetically connected with granitic rocks.

GEOCHEMICAL CYCLE

Germanium is readily extracted from minerals during weathering and transported as soluble salts which are stable in aqueous solution.

Consequently, only a little remains in the resistates. Germanium is precipitated and often enriched in hydrolyzate and oxidate sediments. The germanium content of sea water is very low. The content of germanium in iron ores of sedimentary origin is often somewhat higher than the content in hydrolyzates, whereas the sedimentary manganese ores are devoid of germanium. The germanium content of sedimentary rocks is presented in Table 41.5.

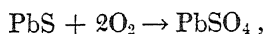
More tin than germanium and lead remains in the resistates because detrital cassiterite, the most common of tin minerals, is highly resistant to weathering. Cassiterite is sometimes concentrated in large alluvial and eluvial deposits which are of high economic importance (Dutch East Indies). The part of tin originally bound within sulfides and silicates is also promptly precipitated after the decompo-

TABLE 41.5
CONTENT OF GERMANIUM IN SEDIMENTARY ROCKS

Rock	Ge (g./ton)
Sandstones, average (Preuss, 1941)	3
Shales, average (Goldschmidt and Peters, 1933a)	5.6
Shales, average (Preuss, 1941)	7
Oolitic iron ores (Palmqvist, 1935)	3.5
Sedimentary iron ores, average (Goldschmidt and Peters, 1933a)	7
Sedimentary manganese ores (Goldschmidt and Peters, 1933a)	0

sition of the minerals in question. Comparatively little is known of the content of tin in sedimentary rocks. It becomes enriched in aluminum-rich hydrolyzates; Goldschmidt and Peters (1933b) report an average of 72 g/ton Sn in bauxites and 40 g/ton in shales. Owing to the low solubility of tin during weathering, its content in sedimentary iron ores is low, 8 g/ton Sn being reported by Goldschmidt and Peters.

Lead, like germanium, is rather readily extracted from its minerals during weathering and transported in the form of soluble stable compounds. The oxidation of galena into lead sulfate,



is rather slow. The process is facilitated by the presence of pyrite, which yields ferric sulfate, thus acting as an oxidizing agent (Schneiderhöhn, 1928). The sulfate of lead is only moderately soluble and therefore does not migrate much. Lead carbonate is formed from lead minerals in the presence of carbon dioxide and bicarbonates; the

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carbonate is still less soluble than the sulfate. It is formed from anglesite by the action of carbon dioxide or soluble bicarbonates and therefore represents the most stable lead compound in the oxidation zone. Phosphates, arsenates, vanadates, and chlorides of lead may also be formed in the oxidation zone. In the zone of reduction, lead is never reprecipitated as sulfide, whereas the silver contained in galena is strongly enriched in these surroundings. Lead bicarbonate is many times more soluble than the normal carbonate, and consequently lead may be transported as bicarbonate. Relatively much lead is present in sea water. It is precipitated, as sulfide, in sediments rich in organic remains and becomes adsorbed and enriched in hydrolyzates and oxidates. The average content of lead in resistates and hydrolyzates is 20 g/ton Pb, and in limestones, 5–10 g/ton (Goldschmidt, 1937*b*). Siebenthal (1915) reported up to 32.6 g/ton Pb in American limestones and dolomites, and Forchhammer (according to Boury, 1938) found as much as 20 g/ton Pb in some corals. Boury reported 1.1 g/ton Pb in marine evaporates. According to Wickman (1948), it is probable that the lead content of limestones and anhydrites is up to 10 g/ton and 1 g/ton, respectively, because the similarity of the radii of Sr^{2+} and Pb^{2+} means that the lead and strontium contents of sea water and of precipitates and evaporates are proportional.

The values discussed above show that the greatest part of the three elements is removed from sea water or never reaches the oceans. This fact is particularly important in the case of lead, because of its strong toxic properties.

BIOGEOCHEMISTRY

Germanium has been found in the ashes of some seaweeds, certain land plants, and some animal tissues. Its physiological role, if any, is unknown, but it is claimed that germanium, particularly when associated with other elements having the same property, stimulates the formation of red blood cells. Germanium is enriched in coal ashes, its maximum concentration being 1.6 per cent GeO_2 (Goldschmidt, 1930*b*; Goldschmidt and Peters, 1933*c*). It is precipitated as bivalent compounds because of the reducing action of coal, and the enrichment is increased still more, owing to the adsorptive properties of the carbonaceous sediments.

Tin is reported in the ashes of some marine animals, e.g., oysters. Small amounts of tin are found in plants and in most tissues of higher

animals. Some bacteria are believed to be able to separate tin from thermal waters. It is sometimes notably enriched in coal ashes.

Lead is present in the ashes of many land and sea plants and is enriched in coal ashes. It is also found in many marine animals, especially corals, Crustacea, and mollusks, and as an erratic microconstituent of higher animals. However, it probably has only a toxicological function.

The maximum content of germanium, tin, and lead in soil, according to Mitchell (1944), is 10, 200, and 1,000 g/ton, respectively.

LEAD ISOTOPES

The three radioactive series derived from uranium, actinouranium, and thorium result in the ultimate formation of the three isotopes of radiogenic lead: Pb^{206} , Pb^{207} , and Pb^{208} , respectively. There exists, in addition, a fourth isotope, Pb^{204} , which is not known to be connected with radioactive disintegration. It is believed to represent primeval lead. The ratios of the lead isotopes show considerable variation. The closest approach to primeval lead is the lead obtained from galena found at Ivigtut, Greenland, with the ratios $\text{Pb}^{208}/\text{Pb}^{204} = 34.5$, $\text{Pb}^{207}/\text{Pb}^{204} = 14.7$, and $\text{Pb}^{206}/\text{Pb}^{204} = 14.6$ (Nier, Thompson, and Murphey, 1941).

ARSENIC, ANTIMONY, BISMUTH

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE three elements arsenic, antimony, and bismuth are notably rare constituents of the upper lithosphere, arsenic being the most abundant and bismuth the rarest of them. According to determinations of Noddack and Noddack (1930, 1934, As, Sb, Bi in meteorites) and of Goldschmidt and Peters (1934, As in igneous rocks; Goldschmidt, 1937*b*, Sb and Bi in igneous rocks), the average contents of these elements in terrestrial and meteoritic material are as shown in Table 42.1.

TABLE 42.1
ABUNDANCE OF ARSENIC, ANTIMONY, AND BISMUTH
IN METEORITES AND IN IGNEOUS ROCKS

MATERIAL	As	Sb	Bi
	g/ton		
Nickel-iron phase of meteorites	360	2 0	0 5
Troilite phase of meteorites	1,020	7 8	2
Silicate phase of meteorites	20	0 1	0 02
Igneous rocks	5	1	0 2

Arsenic and bismuth are absent altogether from the solar atmosphere, whereas the content of antimony has been quantitatively determined. All three elements are considerably enriched in the sulfide phase of the meteorites. Their most prominent feature, as far as general geochemistry is concerned, is their chalcophile character. However, arsenic is also enriched in meteoritic iron. This fact and the presence of 2,300 g/ton As in josephinite and up to 500 g/ton As in other telluric irons (Goldschmidt and Peters, 1934) afford proof of the siderophile character of arsenic.

The geochemistry of arsenic is known relatively well, whereas that of antimony and bismuth is, so far, known very imperfectly. The

abundance values given in Table 42.1 cannot be considered final. They are still far from satisfactory, being largely based on insufficient material.

MANNER OF OCCURRENCE IN IGNEOUS ROCKS; ORES

According to the calculations presented in Table 5.2, arsenic, antimony, and bismuth are oxyphile. No reliable determinations are available to show the content of arsenic in the various groups of igneous rocks. Antimony and bismuth were absent in a composite sample of gabbros analyzed by Preuss (1941); the average contents in granites were 0.3 g/ton Sb and 2 g/ton Bi. With the exception of the rare bismuth silicate, eulytite, $\text{Bi}_4[\text{SiO}_4]_3$, no other silicate minerals are known to contain these elements as major constituents. They readily combine with sulfur, selenium, and tellurium and form sulfosalts, arsenides, and antimonides with various heavy metals, preferably copper, iron, nickel, and cobalt. In the native state the three elements are found in many mineral veins. Arsenic, in addition, forms a number of arsenates which contain the $[\text{AsO}_4]$ anion in a structural position analogous to that of the $[\text{PO}_4]$ group of the phosphates. The arsenates are often isomorphic with the phosphates of corresponding chemical composition. Such is the case, for example, with mimetite, $\text{Pb}_5[\text{Cl} | (\text{AsO}_4)_3]$, which is isomorphic with apatite. The trioxides of the three elements occur in Nature as two different modifications: As_2O_3 as arsenolite and claudetite, Sb_2O_3 as valentinite and sénarmontite, and Bi_2O_3 as bismite and sillénite. Sénarmontite is the most important of these minerals. A number of arsenites are also known as minerals; antimony occurs as oxides, some of which are included in the pyrochlore group; and vanadates, arsenates, tellurates, and molybdates of bismuth are found in Nature. In pegmatites, antimony and bismuth sometimes accompany columbium and tantalum in oxide minerals (see chap. 26).

Only small amounts of the three elements are found in rocks and minerals belonging to the early and main stages of magmatic crystallization. The early magmatic iron ores are low in arsenic. The average minimum content in magmatic sulfides, according to Goldschmidt and Peters (1934), is about 2,000 g/ton As. Therefore, the value 60 g/ton As given by Noddack and Noddack (1931a) might be too low (see Table 5.2) and the oxyphile character of arsenic in the upper lithosphere rather weak. It is probable that notable quantities of arsenic are present in pyrite (Ramdohr, 1940), but certainly very

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much arsenic is found in the phosphate minerals of igneous rocks, chiefly in apatite, in which it replaces phosphorus, and in silicates. Some bismuth is also present in apatite, but this circumstance might be due to the fact that the radius of Bi^{3+} (1.20 kX) closely resembles that of Ca^{2+} (1.06 kX; Goldschmidt, 1937*b*). Only arsenic among the elements in question is present in the early-separated magmatic sulfides in quantities worthy of mention, being found therein, for instance, as sperrylite, PtAs_2 . All three elements, on the other hand, are strongly enriched in the late magmatic crystallates. Notable amounts of arsenic may already have become separated during the pegmatitic stage as arsenopyrite, FeAsS , and loellingite, FeAs_2 . However, not until the pneumatolytic and hydrothermal stages are reached is the greatest number of the independent minerals of these elements met. Arsenopyrite and cobaltite, CoAsS , among many other arseniferous minerals, occur in deposits formed at igneous contacts, and the former mineral is often plentiful in cassiterite deposits. Minerals deposited by volcanic emanations contain arsenic as a common constituent.

Arsenopyrite is the most important mineral of arsenic, whereas the corresponding antimony mineral, gudmundite, FeSbS , is very rare and of no technical value. The corresponding bismuth compound does not occur as a mineral. The economically most important minerals of antimony and bismuth are stibnite, Sb_2S_3 , and bismuthinite, Bi_2S_3 . The corresponding arsenic sulfide—orpiment, As_2S_3 —is of minor importance as a source of arsenic. Realgar, AsS , is the only monosulfide of the three elements found as a mineral. Along with the above-mentioned independent minerals, various sulfide ores contain varying amounts of the three elements, which are recovered as by-products of the metallurgical processes using such ores. Arsenic, antimony, and bismuth are found in galena, but their presence has never been established in pure sphalerites (Ofstedal, 1940). According to Hoehne (1934), a substantial content of arsenic and bismuth in galena is always due to admixed impurities, whereas in the case of antimony, which is greatly preferred by galena, anomalous mixed crystals of antimony minerals, perhaps tetrahedrite, with galena might be present, and the content may be as high as 1 per cent Sb.

The general rule during the separation of the three elements from magma is that arsenic begins to separate at the highest temperatures after the main stage of crystallization, i.e., during the pegmatitic stage. Next comes bismuth, which is separated from relatively hot

hydrothermal solutions. Antimony is the last of the three to crystallize; it often accompanies mercury, particularly in the metalliferous veins of volcanic regions; but the separation of antimony starts somewhat earlier than that of mercury. However, arseniferous minerals are also important constituents in metalliferous veins.

GEOCHEMICAL CYCLE

The cycle of bismuth differs materially from that of arsenic and antimony. Bismuth is comparatively readily precipitated as basic carbonate which is formed during the hydrolytic decomposition of bismuth salts in aqueous solution. Therefore, it becomes enriched in the hydrolyzates. Several carbonates of bismuth occur as minerals, but, because their crystal structures are largely unknown, their classification so far is incomplete. Bismutite, $\text{Bi}_2[\text{O}(\text{OH})_2 | \text{CO}_3]$, is one of the important carbonate minerals of bismuth.

The other two elements possess a tendency to become precipitated in the hydrolyzates as well. They are all enriched in oxidate sediments, chiefly by adsorption on ferric hydroxide. A part is brought down also by the iron sulfide formed by reduction in bituminous oozes. According to Goldschmidt and Peters (1934), the average content of arsenic in argillaceous sediments is of the same degree of magnitude as the average in igneous rocks. The analyses made by B. Fr. v. Bülow (Goldschmidt and Peters, 1934) show an average of 4 g/ton As in the sediments from the bottom of the Atlantic. Goldschmidt and Peters found 65–650 g/ton As in Mesozoic and Paleozoic oxidic iron ores of sedimentary origin, corresponding to an enrichment of about one hundred times the average content in argillaceous sediments. The sedimentary siderite ores are materially lower in arsenic, but the iron-rich bauxites and the glauconitic marine sediments are generally high in this element, which also follows iron in fresh-water oxidates, e.g., lake and bog ores. However, the manganese-rich oxidates are lower in arsenic than are the iron-rich types.

An arsenic content in excess of 3,000 g/ton was reported by Goldschmidt and Peters (1934) in a sedimentogenic pyrite.

During metamorphism, most arsenic is removed from the iron-rich sediments.

Small amounts of arsenic escape precipitation in oxidate sediments and remain in sea water, but the exact manner of occurrence of arsenic in the sea is still unknown. It has been suggested that arsenic is present in sea water chiefly as arsenite. The content of arsenic

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fluctuates because arsenic is able to replace phosphorus in many marine organisms. Therefore, arsenic is present in marine phosphate deposits; Goldschmidt and Peters (1934) report between 0.007 and 0.03 g/ton As in a phosphorite.

As a matter of fact, the sediments and sedimentary rocks of marine origin should contain more arsenic than igneous rocks do, on an average, because much arsenic has evidently been introduced directly into the exogenic cycle by volcanic activity.

Information regarding the exogenic cycle of antimony and bismuth is far from sufficient. Preuss (1941) reports the following average contents:

Sandstones:	1 g/ton Sb and 0.3 g/ton Bi
Shales:	3 g/ton Sb and 1 g/ton Bi

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Arsenic, in small quantities, is a universal contaminant of plants and animals and may sometimes be notably concentrated in organisms, e.g., in land plants growing in soil rich in arsenic and in marine and fresh-water organisms, such as fishes, mollusks, crustaceans, plankton, and some brown algae. Goldschmidt and Peters (1934) found up to 325 g/ton As in the ashes of beech humus (see chap. 8). It has been suggested that arsenic is an essential constituent of living cells. It is often strongly enriched in coal ashes. Therefore, the dust and smoke particles in and around cities and industrial centers are arseniferous. Many pyrites found in coal beds are also high in arsenic. The arsenic brought into the atmosphere by the burning of coal and partly by volcanic activity is finally precipitated in rain water. In normal rain water von Fellenberg (1930) found, on an average, 0.0025 g/ton As.

Antimony is reported to occur in the ashes of seaweeds and marine animals. The degree of its enrichment in these materials is very low. Bismuth is present in some marine organisms. The biological role of antimony and bismuth, if any, is unknown.

SULFUR, SELENIUM, TELLURIUM

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

NEXT to titanium, manganese, and phosphorus, sulfur is the most abundant of the trace elements in the uppermost parts of the lithosphere. Likewise, Figure 2.2 shows that the cosmic abundance of sulfur is higher than that of the elements mentioned. Sulfur is, in addition, more abundant than the alkali metals, calcium, and nickel. Consequently, sulfur is one of the geochemically more important elements. Sulfur, if anything, is geochemically chalcophile, and

TABLE 43.1
ABUNDANCE OF SULFUR, SELENIUM, AND TELLURIUM

SOURCE	S	Se	Te
	g/ton		
All meteorites (Goldschmidt, 1937 <i>b</i>) .	21,200	7	0.1:
All rocks (Goldschmidt, 1937 <i>b</i>) . .	520	0 09	0 0018:

the affinity of other elements for sulfur or their solubility in the iron monosulfide melt will determine the strength of their chalcophile character. Selenium and tellurium, which belong to the same subgroup in the Periodic System as sulfur, are similarly chalcophile, but their manner of occurrence distinguishes them from sulfur in many respects. The S:Se ratios of the various groups of meteorites show that selenium is more strongly siderophile than sulfur is (Goldschmidt and Strock, 1935).

The geochemistry of sulfur and selenium is known comprehensively, whereas that of tellurium is still largely unknown. The abundance of the three elements is presented in Table 43.1.

The values show that the abundance of selenium and tellurium, compared with that of sulfur, is rather low. However, accurate values

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of the abundance of these elements are not readily obtained because the common igneous rocks are notably poor in the three. Clarke and Washington (1924) estimated the content of sulfur in igneous rocks as 520 g/ton; but this value, even though the best one so far available, is not too reliable. Likewise, the abundance values of the other two elements must be considered as tentative. The reason is that sulfur, selenium, and tellurium are strongly enriched in sulfide-ore bodies, the mass of which cannot be accurately determined.

Sulfur has been quantitatively determined in the Sun's atmosphere, but selenium and tellurium are absent therein.

With reference to their terrestrial occurrence, sulfur is also rather pronouncedly biophile, and selenium also seems to share this property in certain respects.

SULFUR IN IGNEOUS ROCKS

A sulfide melt and a silicate melt are only partially miscible, particularly at lower temperatures. Therefore, the sulfides are separated from the magma at an early stage of the crystallization, before the main stage sets in, and a great number of elements having a high affinity for sulfur thus become separated from the magma in the sulfide phase. The main constituent of the separated sulfides is iron sulfide, chiefly pyrrhotite, FeS , which is always deficient in iron (see chap. 5). Along with pyrrhotite, the early-separated sulfides contain notable quantities of pentlandite and chalcopyrite (see below). The general rule is that elements having a higher affinity for sulfur than iron has tend to become enriched in these sulfide segregations, whereas elements with a lower affinity for sulfur remain temporarily in the silicate melt and become more notably concentrated only in late magmatic crystallates. According to Noddack and Noddack (1931a), the average sulfur content of primary magmatic sulfides is 40.4 per cent.

The rocks formed during the main stage of the crystallization contain but little sulfur. Although some silicate and phosphate minerals, such as those belonging to the sodalite-helvite group, the scapolites, and the apatites, contain sulfur in the form of sulfide and sulfate anions, their geochemical importance usually is not high. The rock-making silicates with sulfate anions are met in alkalic rocks and may be considered characteristic constituents of such rocks in some cases. They are noselite (nosean), $\text{Na}_8[\text{SO}_4](\text{AlSiO}_4)_6$, with 8 per cent SO_3 ; hauynite, $(\text{Na}, \text{Ca})_{8-4}[(\text{SO}_4)_{2-1}(\text{AlSiO}_4)_6]$, with 12 per cent SO_3 ; and

lazurite, $(\text{Na,Ca})_8[(\text{SO}_4, \text{S, Cl})_2 | (\text{AlSiO}_4)_6]$, which contains 10.5 per cent SO_3 .

The calculations presented in chapter 5 show that, in igneous rocks, sulfur is nearly quantitatively contained in independent sulfide minerals. It is the prototype of sulfophile elements. As was pointed out in chapters 29, 36, and 41, copper, molybdenum, and lead, in particular, tend to collect all available sulfur during the crystallization to form chalcopyrite, molybdenite, and galena. According to Newhouse (1936) and Ramdohr (1940), the most abundant sulfide minerals in normal igneous rocks are those shown in Table 43.2.

Bornite is rarer than the other four minerals. Pyrrhotite, pentlandite, and chalcopyrite are abundant in basic rocks, e.g., in gab-

TABLE 43.2
THE MOST ABUNDANT SULFIDE MINERALS
OF IGNEOUS ROCKS

Mineral	Composition	Sulfur (Per Cent)
Pyrite	FeS_2	53.5
Pyrrhotite	$\text{FeS-Fe}_9\text{S}_8$	35 4-41 8
Chalcopyrite	CuFeS_2	34 9
Pentlandite	$(\text{Fe,Ni})_9\text{S}_8$	32 7-33 4
Bornite	Cu_5FeS_4	25.6

bro, and also in diorites, whereas pyrite is more often a constituent of acidic rocks. The content of sulfur in the most important classes of igneous rocks is presented in Table 43.3, which is based on the values reported by Tröger (1934). The values show that basic rocks contain more sulfur than acidic rocks do. However, some granites and granite pegmatites may sometimes contain notable amounts of certain sulfides.

When the late magmatic stage of crystallization begins and the pegmatites are formed, more sulfur becomes separated than during the main stage. However, the extensive enrichment of sulfur does not take place until pneumatolytic and hydrothermal stages are reached. In rocks crystallized during these stages sulfur is incorporated in a great number of minerals, and the profusion of such sulfur-bearing species is a feature characteristic of the rocks in question. These pneumatolytic and hydrothermal minerals are sulfides and sulfosalts of metals with a high affinity for sulfur. The part of copper, nickel, and cobalt which is not bound in the early-separated magmatic sul-

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fides is also present in these minerals. It is believed that colloids play an important part in the transportation of sulfides in late magmatic solutions, and complex ions, e.g., $[\text{CuS}_3]^{4-}$, may also be effective.

SELENIUM AND TELLURIUM IN IGNEOUS ROCKS

Selenium and tellurium accompany sulfur in the sulfides separated from the magma. According to Noddack and Noddack (1931a), the selenium content of primary magmatic sulfides is 200 g/ton and the tellurium content 2 g/ton. Like sulfur, selenium and tellurium are pronouncedly sulfophile in the upper lithosphere. The average S:Se ratio in early magmatic sulfides is 2,000:1–20,000:1 (Goldschmidt and Hefter, 1933), and in pneumatolytic and high-temperature hydro-

TABLE 43.3
CONTENT OF SULFUR IN IGNEOUS ROCKS

Rock	S (g/ton)
Peridotites	2,500
Pyroxenites	3,000
Anorthosites	1,000
Gabbros	2,000
Diorites	1,000
Granites	500
Alkalic pyroxenites	2,000
Theralites, essexites	1,000
Syenites, monzonites	500
Nepheline syenites	2,500

thermal sulfides and arsenides the ratio is 400:1–20,000:1 (Goldschmidt and Strock, 1935). On the other hand, selenium is much less abundant in hydrothermal rocks and minerals formed at intermediate and low temperatures—the S:Se ratio is 70,000:1–250,000:1 (Goldschmidt and Strock, 1935). The values of the S:Se ratio show that selenium is enriched preferably in hydrothermal sulfides and arsenides formed at elevated temperatures.

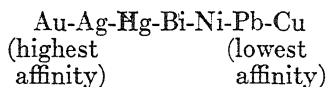
The radii of S^{2-} (1.74 kX) and Se^{2-} (1.91 kX) are alike, and therefore selenium replaces sulfur diadochically in sulfide minerals of igneous origin. The replacement occurs more readily at elevated temperatures than at low ones. In hydrothermal rocks, in particular, selenium forms a number of selenides containing silver, copper, mercury, bismuth, lead, and other elements, and a number of complex sulfosalts; but all these minerals are geochemically relatively rare. Their selenium content may run as high as 48 per cent. Some selenites are also known, e.g., chalcomenite, $\text{Cu}[\text{SeO}_3] \cdot 2\text{H}_2\text{O}$, and the selenites of cobalt and molybdenum; but all such minerals are rare and probably

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are alteration products of selenides. In hydrothermal rocks tellurium, in like manner, forms tellurides of the elements mentioned above and of still other elements. It shows, in addition, a special tendency to combine with gold, which it accompanies in many mineral veins. The gold tellurides, e.g., calaverite, AuTe_2 , and sylvanite, AgAuTe_4 , were discussed in chapter 37. The oxidation products of the telluriferous minerals include various rare tellurites and tellurates, e.g., durdenite, $\text{Fe}_2[\text{TeO}_3]_3 \cdot 4\text{H}_2\text{O}$; ferrotellurite, $\text{Fe}[\text{TeO}_4]$ (?); and teinite, $\text{Cu}[(\text{Te},\text{S})\text{O}_4] \cdot 2\text{H}_2\text{O}$.

Like sulfur, selenium and tellurium are also found in Nature in the native state. They form, in addition, mixed crystals—selen-tellurium, (Se,Te) . The oxides selenolite, SeO_2 , and tellurite, TeO_2 , are oxidation products of the native elements or of selenides and tellurides. Selenium also accompanies sulfur in volcanic emanations. The S:Se ratio of sulfur sublimates of volcanic regions varies from 600:1 to 140,000:1, according to Goldschmidt and Hefter (1933). Thus it is similar to the ratio in sulfides in igneous rocks. The selenium content of native sulfur of volcanic origin may be as high as 5.18 per cent.

According to Ščerbina (Scherbina, 1937), the affinity of tellurium for metals in minerals decreases according to the series



So far, the selenium and tellurium content of the various classes of igneous rocks is unknown.

SULFUR, SELENIUM, AND TELLURIUM IN THE BIOSPHERE

Sulfur is a universal constituent of plants, in which it occurs in the form of inorganic sulfates, organic sulfides, and a large number of organic compounds, e.g., proteins. As a matter of fact, sulfur is essential for the protein synthesis in plants. In the animals, sulfur is assimilated as thioamino acids obtained from sulfoproteins. It is finally oxidized to sulfate in the animal and removed in the excretions.

Sulfur enters into the plants as soluble sulfates, which yield partially reduced organic compounds containing sulfur. Upon further reduction by bacteria in soil or in animals feeding upon plants, these substances yield hydrogen sulfide. This compound is oxidized by bacteria to sulfates, which are partly precipitated in soil and partly enter the plants in a new cycle.

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Sulfur is a constituent of coal ashes. However, sulfide minerals deposited from circulating solutions are present in coal beds, and therefore all the sulfur in the ashes was not originally contained in the plant remains. Some solid bitumens are exceptionally rich in sulfur and they are likewise rich in vanadium; their origin was discussed in chapter 25.

Selenium is related to sulfur in its biological behavior also. Thus plants may take up selenium from soil, and some species are able to enrich selenium. Plants contain selenium both as inorganic selenate and as organic compounds, as a part of the amino acid molecules. Upon analysis, several species yield both inorganic and organic forms of selenium. The ability to incorporate selenium varies strongly in different species. As a rule, plants taking up much sulfur incorporate much selenium as well. Seleniferous plants accumulating available selenium may contain, according to Beath and Eppson (1947), 1,000–2,000 g/ton Se, which is collected from soil with a content of 2–5 g/ton Se. In soil, selenium is adsorbed on the finely divided inorganic and organic colloidal matter. Some plants (*Astragalus*, *Xylorrhiza*, *Oonopsis*, and *Stanleya*) are definitely associated only with seleniferous soils and grow nowhere else. They are primary selenium indicators, whereas other plants, the secondary selenium adsorbers, although not restricted to seleniferous soils, are capable of adsorbing this element from the substratum. In western United States the seleniferous plants are definitely correlated with certain geological formations. The highest selenium content so far reported in a plant is 15,000 g/ton in the locoweed (*Astragalus racemosus*; Beath, Gilbert, and Eppson, 1941).

Animals, unlike plants, are not capable of synthesizing seleniferous amino acids, and it is probable that they cannot convert inorganic selenium compounds into organic ones. In addition, selenium, in contrast to sulfur, is poisonous to most organisms. In higher animals selenium is largely removed as volatile compounds during respiration.

Some autotrophic bacteria oxidize selenium, and such micro-organisms may also reduce selenites. Therefore, selenium may, to some extent, replace sulfur in certain organisms. However, selenium is probably not essential to higher organisms and only follows sulfur in the biosphere.

Selenium is sometimes enriched in coal ashes (Goldschmidt and Hefter, 1933; Goldschmidt and Peters, 1933c), owing to the reducing

action of coal on circulating seleniferous solutions. Selenium is also reportedly a constituent of pyrite found in coal seams.

The biogeochemistry of tellurium seems to be completely unknown.

CYCLE OF SULFUR

During weathering, the sulfide minerals are oxidized, whereby sulfates are produced. Sulfates are also liberated during the decomposition of minerals containing $[\text{SO}_4]$ groups. A part of the sulfates remains in solution, whereas another part is precipitated as sparingly soluble gypsum, barite, and anglesite. The sulfates in solution are brought into the sea or closed continental basins. According to the analyses presented in Table 6.7, the following is the sulfur content of dissolved solids from lake and river waters and from sea water:

Source	S (Per Cent)
Dissolved solids, lake and river water.....	4.00
Dissolved solids, sea water.....	2.53

The values show that the salts of river waters contain nearly twice as much sulfur as the salts dissolved in the ocean. This result is of high geochemical importance because it shows that the two sulfur contents are disproportional. The explanation of the low sulfur content of ocean water lies in the ionic properties of the sexpositive sulfur ion. In sulfates, sulfur is 4-co-ordinated, and therefore hydrogen bond prevails in them (Wickman, 1944; see chap. 5). Consequently, sulfur belongs to the group of the elements forming complex anions with oxygen which are stable in solution. However, the sulfates in solution in the sea share the fate of the carbonates, in that the sulfates of the alkaline-earth metals are only sparingly soluble. A notable part of the sulfate anions becomes separated from the sea in the form of gypsum, $\text{Ca}[\text{SO}_4] \cdot 2\text{H}_2\text{O}$, and anhydrite, $\text{Ca}[\text{SO}_4]$.

Stagnant conditions exist in closed basins which have shallow outlets to the sea and in which lack of circulation causes the loss of oxygen. Under such conditions, the sulfates are partly reduced to sulfides, probably largely by the action of bacteria. In like manner, hydrogen sulfide is formed in stagnant waters from the vegetable sulfur-bearing compounds in the reduction processes caused by bacteria. Stagnant waters are found in some Norwegian fjords, in the Black Sea, in numerous tropical lagoons, and in some salt lakes. In the Black Sea, hydrogen sulfide is found in water from the depth of 180 m downward. At 1,500 m its content is 6.17 ml/l.

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Sapropelic muds rich in organic remains are deposited in stagnant waters, and the presence of hydrogen sulfide causes the precipitation of sulfides of iron and copper in the bottom sediments. Galliher (1933) emphasized the fact that the black sulfide-bearing muds accumulate in an alkaline environment. Ferrous sulfide is considered the precursor of pyrite, which is a common constituent in shales, slates, and schists of sapropelic origin. Such rocks also contain pyrrhotite and other sulfide minerals considered to have been formed in the way just described. The marine black muds usually contain less than 2 per cent iron sulfide and seldom over 5 per cent organic carbon. Newhouse (1927) found that pyrite is the common form of iron sulfide found in sedimentary rocks other than coal, whereas marcasite, FeS_2 , is the main form in coal beds.

Native sulfur is also present in some sediments. In the sea some bacteria reduce sulfates to hydrogen sulfide, which is then oxidized to native sulfur. Other bacteria are capable of depositing sulfur within their cells. Sulfur may also be precipitated when volcanic gases are brought into contact with sea water and fresh water. It may, further, be formed as a product of decomposition of sulfide minerals on the surface and in the zone of weathering and around springs carrying hydrogen sulfide and sulfates in their water.

The cycle of sulfur, with special reference to the biosphere, is presented in Figure 43.1. There are at least three kinds of micro-organisms which have a role in the cycle of sulfur, viz., the autotrophic bacteria, which oxidize sulfides to sulfates in the anaerobic sulfate-hydrogen sulfide phase called sulfuretum; the sulfate-reducing bacteria, which reduce sulfates to sulfides; and the heterotrophic bacteria, which produce hydrogen sulfide from some organic compounds, e.g., proteins (Galliher, 1933).

Table 6.19 shows that the transfer percentage of sulfur is 283, that is, the quantity of sulfur now contained in sea water is nearly three times as high as the amount supplied thereto as a result of weathering processes during the geological history of the Earth. It is therefore obvious that the sulfur now found in the oceans cannot be merely a product of the weathering of rocks. Consequently, there must exist additional sources of sulfur. According to chapters 16 and 44, boron and chlorine are analogous to sulfur in this respect because their present amount in the sea is higher than the quantities transported to the sea in weathering solutions. It is evident that all the elements discussed are brought into the sea by volcanic emanations. The chief

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sulfur compounds present in volcanic gases are hydrogen sulfide and sulfur dioxide. Native sulfur is commonly found in sublimes produced by the volcanic gases, and a number of sulfides and sulfates are also present in these gases. Sulfuric acid and sulfates are the ultimate oxidation products of the sulfur-bearing compounds produced by volcanic emanations. Zies (1929) reported an average content of 0.029

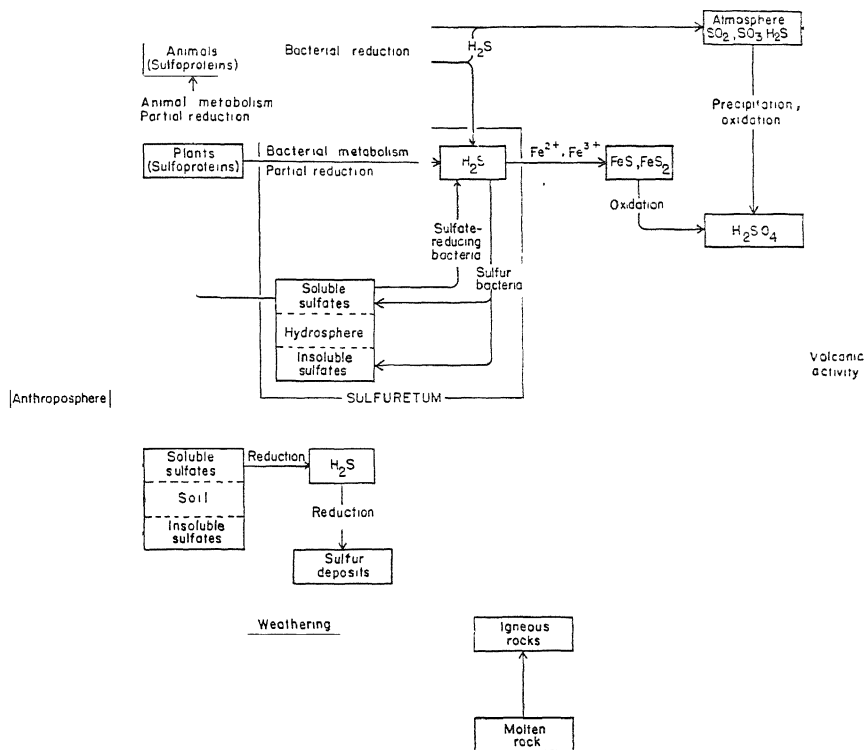


FIG. 43.1.—The cycle of sulfur, chiefly in the biosphere

per cent (by volume) of hydrogen sulfide in the fumarole gases of the Valley of Ten Thousand Smokes in Alaska and approximated the yield of hydrogen sulfide for the year 1919 as $0.3 \cdot 10^6$ tons. Three-quarters of this amount, at least, were added directly to the sea (see also chap. 44).

The amount of juvenile sulfur cannot be readily estimated, but it is evident that it forms a notable contribution to the total of sulfur now present in sea water. It is evident that sulfur is contributed also by the sulfide-ore bodies found in igneous rocks, which are not considered when the average content of this element in igneous rocks is

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calculated. The amount of sulfur produced from the sulfide-ore bodies during weathering cannot be estimated.

According to the considerations presented above, a notable accumulation of sulfur in sea water characterizes the cycle of sulfur. It might be possible that some sulfur has been present in the sea as a primary constituent since the formation of the hydrosphere (Goldschmidt, 1937*a*). The amount of sulfur which is removed by deposition in various sediments is illustrated by the following averages (Clarke, 1924; from analyses of H. N. Stokes):

Rock	S (g/ton)
Sandstones.....	300
Shales.....	2,600
Limestones...	1,100

Because most of the sulfates are leached out from the resistates, the sulfur content of sandstones in this series of analyses is notably low. The greatest part of sulfur either is removed from sea water as sulfates or is reduced to sulfides and deposited in the hydrolyzates. The deposited sulfates consist of those of calcium, strontium, and barium. A considerably smaller part is removed, along with calcium carbonate and magnesium carbonate, in the precipitates. In the evaporates considerable amounts of sulfur are present in the form of huge beds of gypsum and anhydrite, and a small part remains in solution until the last stages of crystallization are reached and forms potassium-magnesium sulfates and double salts with the chlorides that separate from the brines.

On the continents sulfates of sodium, potassium, and calcium are common in evaporate sediments deposited in arid regions on, or immediately beneath, the surface. Some sulfate evaporates, e.g., gypsum, are connected with springs. In many closed basins sulfates, particularly sodium sulfate, are precipitated in noteworthy quantities.

CYCLE OF SELENIUM AND TELLURIUM

The cycles of selenium and sulfur differ widely from each other. The S:Se ratios in some geochemically important materials are listed in Table 43.4.

In sea water selenium, compared with sulfur, is decidedly less abundant than in igneous rocks. According to Table 6.19, the transfer percentage of sulfur is 283, whereas that of selenium is only 7.4. Therefore, it is evident the selenium is removed from the sea to a very much greater extent than sulfur is. The S:Se ratio of argilla-

ceous sediments shows that selenium is already somewhat enriched in the hydrolyzates. In the oxidate sediments the degree of enrichment is still higher. This is caused by the fact that freshly precipitated hydroxides of Fe^{3+} and Mn^{4+} are able to adsorb selenium nearly quantitatively from aqueous solutions. Selenium thus becomes removed from sea water in a manner similar to that of arsenic, i.e., chiefly with depositing oxidates ("depoisoning" of ocean water). Therefore, only a small proportion of all selenium originally brought into solution during weathering remains in the sea. A part of selenium is removed during the precipitation of the carbonate sediments; but the evaporates are nearly entirely devoid of selenium, although they contain

TABLE 43.4

S:Se RATIOS IN SOME GEOCHEMICAL MATERIALS

Material	S:Se
Meteorites (Goldschmidt, 1937b).....	3,000:1
Igneous rocks (Goldschmidt, 1937b).....	6,000:1
Magmatic sulfides (Goldschmidt and Strock, 1935)	10,000:1
Argillaceous sediments (Minami, 1935b).....	4,000:1
Oxidates (Goldschmidt and Hefter, 1933)...	250:1-10,000:1
Sedimentary iron sulfides (Goldschmidt and Strock, 1935)	100,000:1
Limestones (Goldschmidt and Strock, 1935) .	14,000:1
Evaporates (Goldschmidt and Hefter, 1933)..	>500,000:1
Sea water (Goldschmidt and Strock, 1935) .	232,000:1
Nitrate sediments (Goldschmidt and Strock, 1935).....	8,000:1

notable amounts of sulfur as sulfates. This circumstance shows that sulfur and selenium become definitely separated from each other during the exogenic cycle. The sulfur deposits formed by reduction of sulfates in the exogenic cycle contain no selenium at all (Texas and Louisiana in the United States) or only traces thereof (Sicily with a S:Se ratio of 1,000,000:1). The oxidation of the selenide minerals of igneous rocks to selenates, which resemble the sulfates remarkably in their solubility, requires a higher redox potential than the oxidation of sulfides to sulfates. This agrees also with the low heat of formation of selenic acid from SeO_2 , O_2 , and H_2O , as compared with the high value of the heat of formation of sulfuric acid. Accordingly, it is possible that sea water contains selenium in the form of alkali selenites. During the weathering of seleniferous sulfide deposits, selenium is oxidized to selenite, which may form some rare minerals with the heavy metals present in weathering solutions, such as copper, cobalt, and molybdenum. On the other hand, according to Beath, Hagner,

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and Gilbert (1946), water-soluble selenate is the dominant form in the selenium-bearing rocks (tuffs) and soils of Wyoming, and only traces of selenite are present. In the nitrate sediments the redox potential is very high, actually attaining the highest value found in the Earth, and selenium is consequently oxidized therein to selenates, which occur in the company of other oxygen-rich salts, like nitrates, iodates, chromates, and perchlorates. According to Table 43.4, the Chilean nitrate sediments have a S:Se ratio similar to that found in igneous rocks, and no separation of sulfur and selenium has taken place in these deposits.

Both selenates and selenites are readily reduced to selenium or, still more commonly, to various selenides. Some selenium compounds

TABLE 43.5
CONTENT OF SELENIUM IN SEDIMENTS AND SEDIMENTARY ROCKS

Rock	Se (g/ton)
Sandstone, Utah (Beath, Gilbert, and Eppson, 1939)	1 4
Shale, Utah (Beath, Gilbert, and Eppson, 1939) . . .	0.6-96 .3
Limestone, Utah (Beath, Gilbert, and Eppson, 1939) .	0.4- 2 6
Shales, average (Minami, 1935 <i>b</i>)	0.6
Iron sulfides from sedimentary rocks (Minami, 1935 <i>b</i>)	up to 28
Sedimentary copper ores (Minami, 1935 <i>b</i>)	up to 32
Sedimentary iron and manganese ores (Goldschmidt and Strock, 1935)	up to 5.4
Limestones (Minami, 1935 <i>b</i>)	<0.1
Caliche, average (Goldschmidt and Strock, 1935) . . .	5.2

are easily volatile and are therefore found in the atmosphere. They are brought down in precipitation.

Table 43.5 shows the content of selenium in some sediments and in their derivatives. The number of selenium analyses available is still very small. The analyses of Beath, Gilbert, and Eppson (1939) are made of rocks of Provo Canyon, Utah, which are among the most seleniferous sedimentary rocks in western United States. The values show that selenium is concentrated chiefly in the carbonaceous shales. It is a well-established fact that sediments and sedimentary rocks containing much organic matter of vegetable origin are often rich in selenium.

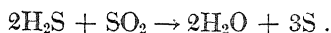
During metamorphism selenium remains, at least partly, in the metamorphic rocks.

Practically no information is available on the cycle of tellurium.

ORES OF SULFUR, SELENIUM, AND TELLURIUM

Native sulfur and various sulfide minerals are used as sulfur ores. Native sulfur is of either volcanic or sedimentary origin. Volcanic

sulfur is produced in the reaction between hydrogen sulfide and sulfur dioxide in the volcanic gases:



The sedimentary sulfur deposits, according to Ahlfeld (1934), are formed chiefly on the border zones of semiarid and arid desert regions in which the sulfates, rather highly concentrated in surface waters, are reduced to hydrogen sulfide, owing to the action of unsaturated hydrocarbons contained in petroleum deposits. Carbon dioxide is also formed in this process, but it is largely bound into carbonates. The hydrogen sulfide migrates upward and is oxidized to sulfur by the atmospheric oxygen. When the supply of hydrogen sulfide becomes exhausted, sulfur is rapidly oxidized to sulfates, and deposits of gypsum, alum, and other sulfates will ultimately be formed. In the absence of the alkali and the alkaline-earth metals, free sulfuric acid may accumulate in the desert soil. Recent sulfur deposits formed by this process are rare, owing to the instability of native sulfur under atmospheric conditions, when the reducing action of the unsaturated hydrocarbons has ceased. Some fossil deposits, such as those in Sicily, in Fergana in central Asia, and in Louisiana in the United States, have been preserved under a cover of sediments.

With the exception of native sulfur, pyrite is the most important ore mineral of sulfur. It is mined expressly for the production of this element. Sulfur liberated during the roasting of sulfide ores is usually collected as well.

Only little selenium is recovered from independent selenium minerals. The element is obtained, instead, as a by-product from flue dusts of certain metallurgical processes which use sulfide ores and from slimes of electrolytic refining processes. Such slimes and the flue dusts from smelters using, in particular, telluride gold ores are the main source of tellurium.

THE HALOGENS: FLUORINE, CHLORINE,
BROMINE, IODINE

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE abundance of the halogens in meteorites and igneous rocks is shown by the values recorded in Table 44.1, which is based on information given by Selivanov (1940, chlorine and bromine in igneous rocks) and Wasserstein (1947, fluorine in igneous rocks), all other values being taken from Goldschmidt (1937*b*). The values recorded in this table show that chlorine is the most abundant of all halogens.

TABLE 44.1
ABUNDANCE OF THE HALOGENS

MATERIAL	F	Cl	Br	I
	g/ton			
Iron phase of meteorites	unknown	unknown	1	0.6
Troilite phase of meteorites	unknown	unknown	unknown	unknown
Silicate phase of meteorites	unknown	800	25	1.25
Meteorites, average	28	1,000-1,500	20	1
Igneous rocks, average	600	314	1.62	0.3

Next to chlorine, fluorine is the most abundant. The remaining halogens—bromine and iodine—run rather low in abundance, bromine being the more abundant of the two.

Chlorine, bromine, and iodine are absent in the Sun's atmosphere, but fluorine is probably present therein. Meteoritic iron contains chlorine as the meteorite mineral lawrencite, FeCl_2 , which has not been encountered in terrestrial rocks.

Geochemically, all the halogens are lithophile elements. When an iron phase is formed in a physicochemical system, a part of the chlorine may, under reducing conditions, enter the metal as ferrous chloride, and consequently it may be possible that this compound is

present in the nickel-iron core of the Earth. With reference to their terrestrial occurrence, all the halogens are present in volcanic emanations. It is possible that the halogens, perhaps with the exception of fluorine, were found in the primordial atmosphere of the Earth, being subsequently condensed and entering the hydrosphere (Goldschmidt, 1926, 1937*b*). During the first separation of phases in the beginning of the geochemical evolution of the Earth, chlorine, bromine, and fluorine were therefore predominantly atmophile. The atmophile character of iodine is still rather pronounced today and is perhaps stronger than its lithophile behavior. That iodine has also a clear, if weak, siderophile and chalcophile tendency was shown by von Fellenberg and Lunde (1927). Furthermore, chlorine, bromine, and especially iodine are biophile. In the upper lithosphere all the halogens are oxyphile.

THE HALOGENS IN IGNEOUS ROCKS

Small quantities of fluorine are nearly always present in igneous rocks formed during the main stage of crystallization. Fluorine is present in mineral structures as univalent F^- ions having a radius (1.33 kX) identical with that of O^{2-} and OH^- (1.32 and 1.33 kX, respectively). The equal size of the fluorine and hydroxyl ions explains the common occurrence of fluorine in silicate minerals containing OH^- groups in their structures; this is another example of diadochic replacement. Fluorine is consequently concealed in micas, amphiboles, tourmaline, etc.

The most common and most important, both geochemically and technically, of the independent fluorine minerals is fluorite, CaF_2 . The simple fluorides of magnesium and aluminum do not occur as constituents of igneous rocks. Sellaite, MgF_2 , is not stable therein, and the many aluminum-bearing fluorides, such as fluellite, $AlF_3 \cdot H_2O$, are but mineralogical curiosities like the rare-earth fluorides, yttrifluorite, $(Ca, Y)F_{2-3}$; tysonite (fluocerite), LaF_3 ; and "yttrrocalcite," $(Ca, Y)F_{2-3}$; the borofluorides, e.g., avogadrite, $K[BF_4]$; and the silicofluorides, such as malladrite, $Na_2[SiF_6]$. The simple sodium fluoride villiaumite, NaF , is extremely rare, but the complex sodium-aluminum fluoride cryolite, $Na_3[AlF_6]$, is technically important. Its principal occurrence is at Ivigtut in western Greenland, where it is mined for use as aluminum ore and as flux in metallurgical processes. Other complex fluorides are formed from cryolite as alteration products.

Like fluorine, chlorine also is nearly always present in igneous

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rocks of the main stage of crystallization in the form of the Cl^- ion. This ion is greater (radius 1.81 kX) than the corresponding fluorine ion, and therefore the two halogens do not usually replace each other in the same mineral but tend to become concentrated in separate species. Chlorine frequently occurs with the complex $[\text{SO}_4]$ and $[\text{CO}_3]$ anions in minerals, e.g., in the chlorosulfate chlorothionite, $\text{K}_2\text{Cu}[\text{Cl}_2|\text{SO}_4]$, and in the chlorocarbonate phosgenite, $\text{Pb}_2[\text{Cl}_2|\text{CO}_3]$. The members of the sodalite-helvite group, the scapolites, and eudialite, $(\text{Na}, \text{Ca}, \text{Fe})_6\text{Zr}[(\text{OH}, \text{Cl})|(\text{Si}_3\text{O}_9)_2]$, are some of the more notable silicate minerals containing chlorine, but their quantitative importance is small. Chlorides, in general, are readily soluble, and therefore there occur no simple chlorides as constituents of igneous rocks. Sal ammoniac, NH_4Cl , is a frequent constituent of volcanic sublimates.

The apatites form a special case; for they are the only minerals in which fluorine and chlorine replace each other and the OH^- and $[\text{CO}_3]$ groups to a considerable extent. As a matter of fact, apatite is the only common rock-making mineral of igneous rocks in which fluorine and chlorine occur as essential structural constituents. In all igneous rocks apatite and certain other accessory constituents are the first minerals to separate out during the crystallization. Kind (1939) showed that fluorine, as a rule, predominates in normal igneous rocks formed during the main stage of crystallization. The F:Cl ratio varies in the rocks; in acidic rocks the content of chlorine decreases with a corresponding increase in the content of fluorine. Therefore, the fluorapatites proper are met in acidic rocks, whereas the apatites of basic rocks are rich in chlorine. However, also in the latter apatites the content of chlorine is lower than that of fluorine. Although apatite is a common accessory constituent of igneous rocks, it is not their chief carrier of fluorine, because the content of fluorine does not increase in proportion to that of phosphorus (Shepherd, 1938, 1940; Barth and Bruun, 1945). Barth (1947) found that in basalts all fluorine is contained in apatite. In other igneous rocks and in metamorphic rocks fluorine is predominantly present in hornblende, micas, and fluorite. Biotite may contain up to 4.3 per cent F. According to Sahama (1945a), fluorite may be a more important source of fluorine in igneous rocks than the other fluorine-bearing minerals. The rapakivi granites of eastern Fennoscandia are higher in fluorine than are granites in general (0.23–0.36 per cent F, according to Sahama), and fluorine is one of the most characteristic constituents of this group of

rocks. Along with fluorine-rich biotite and amphibole, they contain, on an average, 0.5 per cent fluorite.

Fluorine shows a higher tendency to become concentrated toward the last phases of the main stage of crystallization than chlorine, although the tendency in the case of fluorine is not always evident. The concentration of fluorine is most pronounced during the pegmatitic stage and leads to the enrichment of fluorine, as fluorite, in the pegmatites of acidic rocks. Similarly, fluorine is an element peculiar to pneumatolytic and hydrothermal rocks. In pegmatites and contact metamorphic rocks fluorine is often concentrated in topaz, $\text{Al}_2[\text{F}_2|\text{SiO}_4]$, and amblygonite, $\text{LiAl}[(\text{F},\text{OH})|\text{PO}_4]$; pneumatolytic rocks contain the fluorine-bearing micas lepidolite and zinnwaldite.

Bromine is a typical dispersed element in the sense of Vernadsky (1924). It is never considerably enriched in igneous rocks. The ionic radius of Br^- (1.96 kX) is of the same order of magnitude as that of chlorine, and bromine may therefore be expected to be able to replace chlorine in minerals to some extent. The manner of occurrence of bromine in minerals separated during the main stage of crystallization is known very incompletely, but the analyses carried out by de Fellenberg and Lunde (1926) prove, for example, that sodalite, $\text{Na}_8[\text{Cl}_2|(\text{AlSiO}_4)_6]$, does not contain more bromine than do the silicate minerals which are devoid of chlorine as a structural constituent. So far, the form of bromine in the common rock-making minerals is unknown. The maximum bromine content found by de Fellenberg and Lunde was 20 g/ton Br in a labradorite.

Iodine is another example of the typical dispersed elements, and, like bromine, it is never concentrated enough in igneous rocks to form independent minerals. The radius of the I^- ion is 2.20 kX, or considerably greater than that of the Br^- ion. Therefore, the diadochic replacement of the other halogens by iodine is completely out of the question. In some early magmatic sulfides von Fellenberg (1927) found 0.15–0.35 g/ton I. Likewise, the content of iodine in the common rock-making minerals is of a similar degree of magnitude (de Fellenberg and Lunde, 1926). Like bromine, iodine does not follow chlorine in minerals. In addition, the determinations made by de Fellenberg and Lunde showed no noticeable parallelism between the occurrence of bromine and that of iodine in minerals. The highest iodine content reported was 0.94 g/ton I in a hypersthene. The form of iodine in igneous rocks is still unknown; but de Fellenberg and

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Lunde suggest that heavy metals, like copper, silver, lead, and mercury, might combine with iodine to form sparingly soluble iodides.

The content of the halogens in the various groups of igneous rocks is presented in Table 44.2, from which it is evident that the number of determinations available is still too small to be satisfactory. Many

TABLE 44.2
CONTENT OF THE HALOGENS IN IGNEOUS ROCKS

Rock (Troger, 1934)	F Average (g/ton)		
Amphibole rocks	3,000		
Anorthosites, peridotites, pyroxenites .	100		
Gabbros	300		
Diorites, granodiorites	200		
Granites	500		
Alkalic pyroxenites	1,500		
Melilitic rocks	1,500		
Malignites, shonkinites	1,500		
Nepheline syenites	800		
Monzonites	1,000		
Syenites	600		

Rock (Selivanov, 1940)	Cl Average (g/ton)	Br Average (g/ton)	Cl:Br Average
Basalts	260	2 67	131
Gabbros	200	2 00	105
Granodiorites	540	2 57	292
Granites	330	1 60	275
Syenites	400	1 07	284

Rock (de Fellenberg and Lunde, 1926)	I (g/ton)		
Basalt, Siebengebirge, Germany . .	0 31		
Anorthosite, Ekersund, Norway . .	0 23		
Granite, Fredrikshald, Norway . .	0 20		

of the earlier fluorine determinations are unreliable, and new determinations by modern methods are few. However, it is known that fluorine tends to become concentrated in some rocks. Alkalic rocks tend to be high in fluorine, and the obsidians, according to Shepherd (1935), are usually rich in fluorine (up to 0.68 per cent F). Zies (1924) reported up to 7 per cent F in fumarolic incrustations of the Valley of Ten Thousand Smokes. Selivanov (1940) found that the various igneous rocks differ very little in their chlorine and bromine content. On the other hand, the Cl:Br ratio varies, being lower in basic rocks.

The average Cl:Br ratio for igneous rocks is 243. In volcanic sublimates the ratio exceeds the value 300. The content of iodine does not change materially during the differentiation.

BIOGEOCHEMISTRY OF THE HALOGENS

Fluorine is a microconstituent of plants, but some species may accumulate it, for example, tea plants. The potassium salt of monofluoroacetic acid is present in *Dichapetalum cymosum* as a toxic principle; the fluorine content of this plant may run as high as 150 g/ton F. It is also concentrated in coal; according to Robinson and Edgington (1946), many soft coals may contain as much as 100 g/ton F. However, it seems to be possible that the fluorine content sometimes is due to deposition from circulating solutions. Fluorine is also frequently present as a microconstituent in marine animals, which actually are richer in fluorine than are terrestrial species. Marine shells probably contain fluorine as calcium fluoride. In higher animals fluorine is contained in bones and especially in teeth. However, the physiological role of fluorine is still largely unknown. In man and laboratory animals fluorine in high concentrations (>1 g/ton in drinking water and food) causes dental fluorosis, whereas in low concentrations (<1 g/ton) it makes the dental enamel highly resistant to acids, evidently due to the formation of fluorapatite.

Chlorine is found in all plants with the exception of the conifers. Some species are known to secrete sodium chloride, and others tolerate high contents of chloride ion in soil; thus, e.g., *Nitraria schoberi* tolerates sodium chloride in concentrations of 50–80 g/l. Chlorine is also always present in animals. Its content is greatest in lower marine animals and lowest in some fresh-water species. The skeletal parts of anthozoans are reported to contain 0.3 per cent Cl, 4.2 per cent Br, and 6.9 per cent I; in these animals the abundance ratio of the halogens in sea water has been reversed. Chlorine in plants and animals is predominantly inorganic. Certain aromatic chloro-compounds are found in lichens and molds growing in solutions containing inorganic chlorides; but, on the whole, the number of organic chlorine compounds, like that of other organic halogen compounds, is very small. The biological functions of chlorine are versatile. It is a factor in plant growth, a constituent of gastric juice, and a transport element for metals of biochemical importance. In addition, chlorine, together with sodium, has an important function in determining the amount

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of water in tissues and the osmotic pressure in tissue fluids. In cells, chlorine is a buffer agent.

Land plants may contain bromine as a minor constituent, but its role therein is still unknown. Bromine is also a microconstituent of higher animals, but its physiological significance is unknown, and it is possible that it accompanies chlorine only as a ballast element (chap. 8). Bromine is always found in marine plants and animals. The ashes of marine plants may contain nearly as much bromine as chlorine. In anthozoans, bromine may almost completely replace chlorine. There are two organic bromine compounds of biological importance, viz., dibromotyrosine in horny corals, algae, sponges, and annelids, and dibromoindigo, the classical Tyrian purple dye, in the gastropods *Murex brandaris* and *M. purpureus*.

Iodine is a microconstituent of all plants and animals. Its influence in plants is unknown, and it may be only a ballast element. Fresh-water plants contain more iodine than land plants do. According to Cauer (1938), plants may take directly from the atmosphere in excess of 60 per cent of the iodine that they require. Iodine is known to become concentrated in coal ashes. In the sea, marine plants, especially the seaweeds, are very rich in iodine. According to Cauer (1938), leaves of the alga *Laminaria hyperborea* may contain up to 11,476 g/ton I per dry weight. The form of iodine in seaweed is still unknown. Among marine animals some sponges and corals are very rich in iodine, and its content may run as high as 8 per cent of the weight of dry tissue. In horny sponges and horny corals iodine is present in the aromatic amino acid 3,5-diiodotyrosine (iodogorgonic acid) in the skeletal protein. In higher animals iodine is an essential microconstituent. In the thyroid gland of mammals it occurs in the amino acid thyroxine and controls the rate of metabolism. It has, consequently, a very important physiological function in the higher animals. Mason (1938) has emphasized the scantiness of iodine as the factor which prevents its becoming a normal ingredient of proteins, contrary to sulfur and phosphorus.

CYCLE OF THE HALOGENS

The most notable feature in the cycle of the halogens is the fact that they form few insoluble salts. Therefore, they do not become readily precipitated under the conditions of the exogenic cycle.

The cycle of fluorine is shown in Figure 44.1. Fluorite, the most common of fluorine minerals, is rather resistant to weathering. Be-

cause its specific gravity is somewhat higher than that of the common rock-making minerals quartz, feldspars, and micas, it is often concentrated, together with other heavy minerals, in the resistates and may be present in placers. Layers rich in fluorite may sometimes occur in sandstones. A part of fluorite is, however, dissolved, and fluorine is transported into the sea as soluble alkali fluorides. Some fluorine, on its way toward the sea, may be precipitated as calcium fluoride. Little is known about the role of fluorine in the sea. The solubility of calcium fluoride increases in the presence of carbon dioxide, and therefore sea water is not saturated with respect to calcium fluoride.

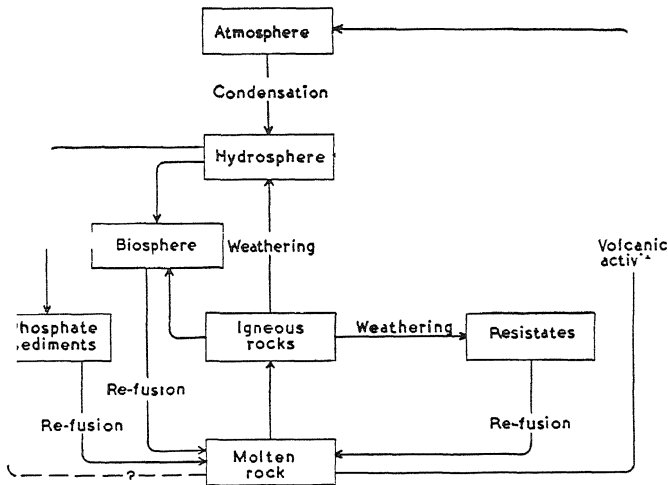


FIG. 44.1.—The cycle of fluorine

Finally, fluorine is deposited in evaporate sediments, in which it may enter the sodium chloride structure. Sellaite is found in potassium salt beds.

The values presented in Table 6.19 show that only a negligible part of fluorine transported into the sea is present in sea water and that the bulk of fluorine is removed from the seas. Calcium fluoride is removed by coprecipitation with barium sulfate, calcium carbonate, and calcium phosphate and consequently enters into many marine sediments. Organogenic phosphates are rich in fluorine. The North African phosphates, on an average, contain 3.5 per cent F. Fluorapatite-resembling minerals are present in the phosphates, and they bring fluorine back to the endogenic cycle (Barth, 1947). Although fluorine and phosphorus are closely related to each other in sediments

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and sedimentary rocks, they gradually become separated during metamorphism and anatexis. The deposition of fluorine in phosphates may also take place in inland waters. The details of the extraction of fluorine are still unknown.

Much of the fluorine found in silicate minerals, particularly in micas, enters the fine-grained transported insoluble residues and the hydrolyzates. It is encountered in the clay minerals. Fluorine is strongly adsorbed in soil. According to Robinson and Edgington (1946), much fluorine is present in the common soil minerals, muscovite, biotite, and hornblende; but, in general, the main source of fluorine in the ordinary soil consists of clay minerals (up to 7,400 g/ton F in bentonite). Fluorine accumulates in cultivated soil as a result of superphosphate fertilization. According to MacIntire, Winterberg, Thompson, and Hatcher (1942), calcium fluoride is the stable form of fluorine in soil in humid regions. They found an average content of 141 g/ton F in normal soil; the average reported by Robinson and Edgington (1946) is 292 g/ton F.

Considerable quantities of fluorine are added directly to the exogenic cycle by volcanic processes. Tagueva (1942) found up to 10.4 g/ton F in natural waters connected with volcanic activity, whereas the maximum content in normal surface water was 2.1 g/ton. Zies (1929, 1938) calculated that the amounts of hydrochloric acid and hydrofluoric acid emitted by the fumaroles of the Valley of Ten Thousand Smokes in Alaska in 1919 were $1.25 \cdot 10^6$ tons and $0.2 \cdot 10^6$ tons, respectively. At least three-quarters of these amounts were added directly to the sea through the action of atmospheric agencies.

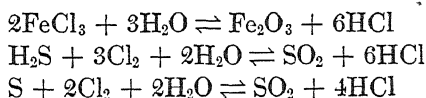
Shepherd (1935) found 1,100 g/ton F in a bottom mud from the Pacific Ocean. Barth and Bruun (1945) reported the following averages: 250 g/ton F in Ordovician limestones, 510 g/ton in Ordovician and Cambrian shales, and 690 g/ton in hornfelses.

The values for the hornfelses show the increase in the content of fluorine with the degree of contact metamorphism.

Chlorine goes readily into solution during the weathering as alkali and alkaline-earth chlorides, etc. When the chloride solutions are brought into contact with heavy metals, particularly mercury, silver, copper, and lead, in the superficial parts of ore bodies, insoluble or sparingly soluble chlorides of the metals in question will be precipitated, e.g., chlorargyrite, AgCl ; cotunnite, PbCl_2 ; nantokite, CuCl ; calomel, HgCl ; and a number of other chlorides, oxychlorides, and

hydrous chlorides. The bulk of chlorine is carried into the sea, where it remains as the chloride ion. Only a small part of the chlorine found in the oceans will finally crystallize in the evaporates as halite, NaCl, and a number of other salt minerals. Halite is the technical source of chlorine.

An important feature in the cycle of chlorine is the fact that many times more chlorine is now present in sea water than has been released by the weathering of rocks and transported into the oceans during the geological history of the Earth (see Table 6.19). This circumstance was explained by Goldschmidt (1937*b*), who claimed that the greatest part of chlorine found in sea water has been liberated by volcanic emanations directly into the hydrosphere. Consequently, only a small part of the chlorine present in sea water has been produced by the weathering of rocks. The analyses of volcanic gases referred to in chapter 5 and above ("Cycle of Fluorine") afford material proof of the validity of this opinion. Hydrochloric acid is present as a common constituent of volcanic gases, in which it may originate in a number of reactions, as, for example, the following (Zies, 1929):



Zies (1929) calculated that the Valley of Ten Thousand Smokes provided about 1 per cent of the total amount of hydrochloric acid needed annually to make up the difference in the Na:Cl ratio in river and ocean water. E. S. Shepherd (according to Zies, 1929) calculated that the volcano Kilauea in Hawaii gives off annually $30 \cdot 10^6$ kg HCl into the atmosphere.

The content of chlorine in sediments and sedimentary rocks is practically unknown. In soil and peat the chlorine content, according to Selivanov (1940), is of the same order of magnitude as in igneous rocks. Compared with bromine and iodine, chlorine appears not so highly concentrated by organic processes.

Like chlorine, bromine also is easily dissolved during the weathering. The bromide solutions may also precipitate heavy metals, whereby insoluble minerals are produced, e.g., bromargyrite, AgBr. Bromine goes, for the most part, into the sea, and its content therein is considerably higher than that of fluorine and iodine. The Cl:Br ratio in sea water is 292. When compared with the Cl:Br ratio in igneous rocks, viz., 243, this value shows the relative enrichment of chlorine

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in the sea. Bromine is concentrated in marine organisms, and thereby it becomes enriched in marine muds and phosphates of organic origin. During the formation of marine evaporates, bromine remains in the mother-liquor until relatively late stages of crystallization are reached. It is subsequently concentrated in the K-Mg salts, in which it replaces chlorine diadachically. In the waters of closed basins and in the evaporates formed therein, bromine is, in addition, strongly enriched in regard to chlorine. Considerable amounts of bromine are often present in brines associated with petroleum. The bromine was an original constituent of the organic substances converted into pe-

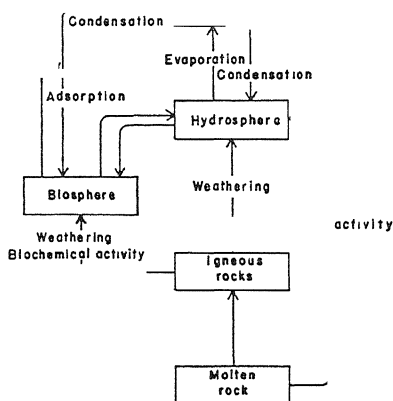


FIG. 44.2.—The cycle of iodine

troleum. Notable underground deposits of bromine are found in the Middle East, from which inorganic bromides are believed to be leached out by underground thermal waters, which finally bring the bromine into the Dead Sea (see chap. 6). It has been suggested that these bromides come from sediments containing the fossilized remains of purple snails. The chief industrial sources of bromine are natural brines, sea water, salt deposits, and the bitters obtained during the evaporation of sea water.

Bromine is concentrated in the soil, and almost all bromine present therein is in organic combination. Selivanov (1940) gives 6.51 g/ton Br as the average content in soil, and 30 g/ton as the average in peat. The bromine content of sediments and sedimentary rocks is not well known. According to Goldschmidt (1937b), the average content in sedimentary rocks is about 3 g/ton Br. Krejci-Graf and Leipert (1936) analyzed a number of sediments and sedimentary rocks for

their bromine content. No difference was found between the bromine content of marine and that of fresh-water sediments. The content of bromine increases in relation to the content of organic matter. During metamorphism bromine is removed, and highly metamorphosed rocks are entirely devoid thereof. According to Krejci-Graf and Leipert, the hydrolyzate sediments contain 0.2 g/ton Br and up; a content of 132 g/ton Br was found in the oil shale (kuckersite) from Estonia, originally an algal mud. The average bromine content in petroleum was approximately 2 g/ton.

The cycle of iodine is presented in Figure 44.2. More details of the cycle of iodine are known than of those of the other halogens. According to the table presented by Goldschmidt (1933*a*, 1934), the content of iodine in igneous rocks, sea water, and other materials of importance in the exogenic cycle of matter is given in the accompanying table.

Material	I (g/ton)
Igneous rocks	0.3
Cultivated soil	2
Air	0 0005
Rain water	0 001 -0.003
River water	0 0007-0.003
Sea water	0.05

Notable amounts of iodine are present in the atmosphere, obviously as vapors of the native element. The content of iodine is higher in air masses of marine origin than in those originating over the continents. Iodine is carried away from the atmosphere partly by rain water and partly by direct adsorption into the soil and into plants. It becomes very strongly enriched in soil as readily soluble compounds. The highest concentration of iodine is found in cultivated soil. According to Goldschmidt (1933*a*), there exists an equilibrium between the iodine adsorbed from the air into the humus-bearing superficial layers of the soil and the portion extracted from the soil by surface water and ground water. Goldschmidt thought it rather probable that the equilibrium has so far not always been attained in geologically young soils, for example, in the once glaciated areas of Fennoscandia and North America. This fact evidently has a high practical importance when the physiological role of iodine is considered. Cauer (1938) showed that very considerable quantities of iodine are released into the atmosphere during the recovery of iodine from the seaweeds by primitive methods. This source of atmospheric iodine is of high physiological importance. A part of iodine returns into

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the sea from the soil. Approximately a fourth of the total amount of iodine remains in the oceans (see Table 6.19).

At least a part of iodine is present in sea water as iodide and iodate, and other forms may also be found. The content of iodine seems to have some relation to the salinity of sea water. It increases parallel to the rise in salinity. Thus, for instance, the iodine content of Red Sea water is high (0.66 g/ton), whereas the Baltic is very low in iodine (0.01 g/ton).

Part of the iodine present in rocks is dissolved as iodide during weathering. Sometimes, when iodine-rich solutions are brought into contact with heavy metals, insoluble compounds may be precipitated, as in the case of chlorine and bromine. Among the minerals formed in the superficial parts of ore bodies of heavy metals, iodargyrite (iodyrite), AgI , and marshite, CuI , deserve special mention. Some secondary lead minerals, e.g., pyromorphite and wulfenite, are particularly rich in iodine (de Fellenberg and Lunde, 1926). However, the possibility of the inorganic concentration of iodine is very small, and all economically important sources of this element were formed by ancient biochemical processes.

Much iodine is removed from sea water by the action of various organisms, particularly the seaweeds, which form an industrial iodine source of high importance. The content of iodine in marine organisms may be as much as 10^5 times as high as its content in sea water. The biological enrichment of iodine results in the low content of iodine in the shallow coastal waters, as compared with the open ocean. It is known (Vinogradov, 1943) that the concentration of iodine by seaweeds and particularly by plankton diatoms creates the necessary conditions for the accumulation of iodine in marine muds. During metamorphism, iodine (as well as bromine) is dissolved in water from these muds and becomes concentrated in mineral waters. The occurrence of iodine in petroleum brines is caused by similar processes (see chap. 8).

Bituminous sediments are comparatively rich in iodine, and the organogenic phosphate deposits and many coals contain noteworthy amounts of iodine. It is rather strongly concentrated in hydrolyzates; the adsorption is promoted by the presence of organic matter. However, the content of iodine in sediments and sedimentary rocks is nearly totally unknown. Goldschmidt (1937b) estimated that sedimentary rocks, on an average, contain 0.8 g/ton iodine. A content of 0.07–0.55 g/ton I is reported to occur in limestones (de Fellenberg

and Lunde, 1926). Among the marine evaporates, particularly the potassium salts devoid of magnesium are regularly iodiferous. However, the ferric compounds contained in these salt sediments as impurities are known to promote catalytically the separation of iodine.

Iodine is strongly concentrated in some evaporates, viz., in the nitrate sediments (see chap. 23). Thus, for example, the Chilean nitrate deposits are comparatively rich in iodine (200–1,700 g/ton I; average 1,500 g/ton). The nitrate beds are, as a matter of fact, the only places where abundant solid iodine compounds are found. Owing to the high oxidation potential prevailing in these deposits, iodine is found there in the form of iodates, the most important of which is the calcium iodate, lautarite, $\text{Ca}(\text{IO}_3)_2$. The origin of these deposits is still a matter of controversy, and no single hypothesis has met all the known facts. It has been suggested that iodine becomes enriched in the nitrate deposits by an adsorption process similar to the phenomena causing its concentration in cultivated soil. Because the adsorption takes place in arid regions, the transportation of iodine is prevented, and therefore it becomes enriched in the nitrate beds, with subsequent oxidation to iodate.

Some mineral waters are rich in iodine, particularly those connected with oil-bearing beds. Such waters are used as industrial sources of iodine, e.g., those on Java with a maximum content of 150 g/ton iodine.

THE INERT GASES

ABUNDANCE AND GENERAL GEOCHEMICAL CHARACTER

THE group of the inert gases includes the following: helium, neon, argon, krypton, xenon, and radon. Radon, being a short-lived radioactive element, will be discussed in chapter 46. The geochemistry of these elements differs from that of other elements in that these gases are chemically highly inert. This property has caused the adoption of the names inert or noble gases for the whole group. So far, no conclusive proof has been presented of the existence of compounds of all the inert gases. However, helium at least may react in spark discharges at high temperatures with a number of elements to form several rather unstable compounds. Owing to the lack of compounds stable under natural conditions, the manner of occurrence of the inert gases, in particular that of helium, may be studied only with respect to substances which accompany them in Nature.

The inert gases are all typically atmophile. They are only sparingly soluble in water and only very little absorbed by solid phases.

Helium is present in the Sun's atmosphere, whereas the other inert gases are absent therein. Although no neon lines are present in the solar spectrum, neon occurs as a constituent of the hotter stars and of the nebulae. Consequently, neon is not a rare element cosmically.

Helium is, next to hydrogen, the most abundant constituent of the Sun. The main-sequence stars have a chemical composition identical to that of the Sun. The high cosmic abundance of helium (see Tables 2.3 and 2.4) is explained by the energy-producing thermonuclear processes which take place in the interiors of the stars and constantly change hydrogen into helium (see chap. 2). Together with hydrogen, helium is cosmically the most abundant of all elements.

Helium is a constituent of meteorites. The greatly varying helium content of the meteoritic irons was explained by Bauer (1947) as a result of cosmic radiation, which has produced extra helium in the

small meteoroids. Cosmic radiation causes nuclear disruptions in which α -particles are among the disintegration products.

Another name used of the elements of this group is the rare gases. With the exception of the short-lived radioactive elements, some of the inert gases are among the rarest of all elements of the Earth. The abundance values of the inert gases in igneous rocks are presented in Table 45.1 and their abundance in the atmosphere in Table 45.2.

TABLE 45.1

CONTENT OF THE INERT GASES IN IGNEOUS ROCKS

Element	Content (g./ton)
He (Goodman and Evans, 1944).....	0.003
Ne (Lord Rayleigh, 1939).....	0.00007
Ar (Lord Rayleigh, 1939).....	0.04
Kr	unknown
Xe.....	unknown

TABLE 45.2

CONTENT OF THE INERT GASES IN THE TROPOSPHERE

Element	Percentage by Volume (Paneth, 1939)	Amount (g. cm ⁻³) (Goldschmidt, 1937b)
Helium.. ..	5.24·10 ⁻⁴	0.0007
Neon . . .	1.8·10 ⁻⁵	0.012
Argon . . .	0.93	12.9
Krypton .. .	1·10 ⁻⁶	0.003
Xenon	8·10 ⁻⁶	0.000045

HELIUM

Radioactivity plays an important role in the geochemistry of helium. Unlike the other inert gases, helium is formed as an end-product of radioactive decay. It is produced in the disintegration of uranium and thorium, the rates of production being $1.16 \cdot 10^{-7}$ ml He per gram of uranium and $2.43 \cdot 10^{-8}$ ml per gram of thorium per year. The independent thorium and uranium minerals are consequently particularly rich in helium. The absolute geological age of such minerals may be calculated if their uranium, thorium, and helium content is known, as was suggested by R. J. Strutt (Lord Rayleigh) in 1910. However, usually at least some of the helium formed has been lost, and therefore the method does not yield reliable results. In igneous rocks the helium content never exceeds the order of 10^{-4} ml per gram, but some radioactive minerals may contain very high

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amounts of helium (up to 10.5 ml per gram in thorianite). Such minerals are, however, rare, and therefore most of the helium seems to be formed in minerals like zircon and sphene, which are common as accessory constituents of igneous rocks and usually contain small amounts of radioactive elements concealed in their structures. Helium is not excessively localized in rocks. Some common rock-making minerals do not retain all the helium generated in their structures during the geological history of the Earth. According to Keevil (1941), the retentivity of feldspar is very low, whereas minerals with close-packed structures, such as magnetite, pyroxenes, and amphiboles, appear to retain helium. Magnetite has a higher helium retentivity than pyroxenes and feldspars. The size of the helium ion is large compared with the vacant spaces in the structures of minerals.

Sometimes excess helium is present in ferromagnesian minerals and in magnetite, either original or added, magmatic or from other sources. Beryls often contain helium in quantities considerably in excess of those which can be accounted for by the traces of radioactive elements present. This remarkable fact is still unexplained (Fay, Glückauf, and Paneth, 1938), but it might be possible that helium is also produced in Nature by atomic transformation processes similar to those which are caused artificially. Such processes might be responsible for the presence of helium in beryl and perhaps in some natural gases (Paneth, 1938). The occurrence of helium in salt minerals (halite and sylvite) is explained by the presence of the lead isotope Pb^{210} (RaD) in these minerals. It produces helium indirectly during its decay.

Helium is, further, identified in the firedamp of many coal mines, in gases from mineral springs, in volcanic gases, and in petroligenic natural gas. As much as 6 per cent He by volume is reported in a mine gas from Sweden (Grip and Ödman, 1944). Here helium is of radiogenic origin. The gases of coal mines may contain up to 0.22 per cent helium by volume, and the gases from some mineral waters in central France contain 10.31 per cent. The cause of the occurrence of helium in such gases still remains to be explained. Very notable helium contents may be found in petroligenic natural gas, the maximum being 16 per cent He by volume in natural gas from the eastern slope of the Rocky Mountains in the United States. However, noteworthy helium contents have been found only in the nitrogen-rich gases, and, even among these, gases containing more than 1 per cent He are relatively uncommon.

The most important helium deposits of the world are the petrogenic natural gas fields of the United States. The total helium reserves in the United States are estimated at over $200 \cdot 10^6 \text{ m}^3$. The Rocky Mountain province mentioned above probably contains the most important of the known industrial sources of helium. As pointed out by Szelényi (1941), the geological age of these deposits is relatively ancient (Carboniferous), and this characteristic is shared by similar deposits elsewhere. Most of the helium was evidently produced by radioactive processes in the country rock, but some may also have come from the organic substances responsible for the formation of petroleum and natural gas. The release of helium from minerals and rocks is greatly promoted by leaching with hydrogen, methane, and its homologues, and it is also activated by the oxidation of rocks during the weathering. These processes are held responsible for the accumulation of helium in natural gas. The presence of helium in volcanic gases is due to its liberation when the rocks react with hot gases and vapors. The presence of methane, hydrogen, and hydrogen sulfide in such gases makes the leaching of helium probable.

Along with helium generated by the radioactive decay, some helium might be present which is original, having never been associated with radioactive elements. There might also be helium which was formed during the radioactive decay prior to the formation of the solid crust of the Earth. Provided that all helium now found in the atmosphere is radiogenic, that the age of the solid lithosphere is $2,000 \cdot 10^6$ years, and that the Th:U ratio therein is 3:1, all helium of the present atmosphere would have resulted from the decay of $2 \text{ kg} \cdot \text{cm}^{-2}$ of average igneous rock, which contains $0.007 \text{ g} \cdot \text{cm}^{-2}$ U and $0.021 \text{ g} \cdot \text{cm}^{-2}$ Th (Goldschmidt, 1937*b*). According to Goldschmidt, however, the amount of igneous rocks required is only 1.3 per cent of the grand total of igneous rocks weathered during the geological history of the Earth. Although there is somewhere in the stratosphere a region in which helium becomes enriched (Paneth, 1938; see chap. 7), it is evident that the quantity of helium liberated during the weathering of igneous rocks throughout the geological evolution of the Earth is many times higher than the present amount of atmospheric helium. Therefore, helium must escape into interplanetary space (see chap. 7).

Other calculations have revealed that the uranium and thorium found in granitic rocks have produced, during the last $1,500 \cdot 10^6$ years, two thousand times as much helium as is now found in the atmosphere. Rogers (1921) estimated that somewhere between 8 and 30

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million m^3 of helium is generated annually by radioactive decay. Because the total helium quantity is approximately 10^{14} m^3 , an amount equal to the present helium content of the atmosphere would be added to it every 10 million years or so (Paneth, 1938). This is another proof of the fact that helium constantly dissipates into the void.

The light helium isotope, He^3 , is very much scarcer than He^4 . Because He^3 must be lost from the atmosphere more readily than He^4 , one would expect this isotope to be concentrated in the upper lithosphere, but actually just the reverse is the case. According to Goodman (1942), the primordial helium in the lithosphere is diluted by radiogenic He^4 , or He^3 is formed in the atmosphere by cosmic radiation.

Helium-bearing petroligenic natural gas is the most important commercial source of helium. The extraction of helium from air is normally prevented by the high cost of the process.

NEON

Neon is found in the atmosphere, being released during the weathering of igneous rocks. According to Lord Rayleigh (1939), neon in igneous rocks is probably trapped in open spaces of mineral structures. The neon content of igneous rocks is presented in Table 45.3, which is based on analyses carried out by Lord Rayleigh.

The values presented in Tables 45.1, 45.2, and 45.3 show that neon is very much scarcer than argon. The Ne:A ratio in the atmosphere is $1.94 \cdot 10^{-3}$. In other words, argon is nearly 520 times as abundant as neon in the atmosphere. According to Lord Rayleigh (1939), the Ne:A ratio in igneous rocks varies from $2.1 \cdot 10^{-3}$ to $6.5 \cdot 10^{-3}$, the average being $4.0 \cdot 10^{-3}$. Therefore, there is no considerable difference in this ratio in the air and in the upper lithosphere. Russell and Menzel (1933) emphasized the fact that neon is cosmically an abundant element, whereas argon is rather deficient. To explain the discrepancy between the cosmic and the terrestrial abundance of these gases, they assumed that the Earth has lost practically all its initial neon into interplanetary space, like most of the hydrogen and the bulk of helium. This suggestion does not agree with the theoretical investigations of Jeans (1925), which showed that, even at temperatures as high as 400° K ., in the upper atmosphere the loss of hydrogen is small and that of all other (heavier) gases negligible. However, Russell and Menzel pointed out that fast-moving gas molecules must

be more abundant in the upper atmosphere than the kinetic theory of gases predicts. They arise from collisions between normal and excited atoms. Oxygen atoms in the metastable state are normal constituents of the upper atmosphere. When they collide with hydrogen and helium atoms, a speed exceeding the escape velocity will be imparted to the two light atoms. Collisions with heavier atoms produce velocities too low for escape. Russell and Menzel emphasized that most of the loss of hydrogen and helium occurred during the first few years of the independent existence of the Earth, the loss of hydrogen being practically immediate. Argon, nitrogen, and neon in the Earth's atmosphere are probably primitive, whereas water vapor and carbon dioxide are juvenile and oxygen is a product of vegetation

TABLE 45.3
CONTENT OF NEON AND ARGON IN IGNEOUS ROCKS

Rock	Ne (10^{-8} ml/g)	A (10^{-5} ml/g)
Eclogite	6.6	2.2
Dunite (average)	8.6	2.2
Granite (average)	6.9	2.4
Obsidian	8.6	1.8

during the later stages of the evolution of the Earth. Russell and Menzel concluded that neon escaped from the atmosphere when the temperature still was very high. A similar conclusion was reached by Goldschmidt (1937*b*), who, however, emphasized the difficulty caused by water vapor, a lighter gas than neon. The dissipation of neon would mean that water vapor has also escaped, and therefore the present hydrosphere would have been produced by degassing only after the escape of neon.

The analyses of Lord Rayleigh (1939), however, show that notable amounts of neon and argon are incorporated in igneous rocks. The predominance of argon among these gases, just as in the atmosphere, does not much favor the view that an excess of primordial neon has been lost from the atmosphere. On the other hand, Unsöld (1941) found neon cosmically nearly as abundant as oxygen and nitrogen (see Table 2.4), and therefore he concluded that the Earth's atmosphere really lost most of its neon at an early stage in its history.

Air is the only commercial source of neon.

ARGON

Argon is found in minerals and rocks, mineral waters, mine gases, volcanic emanations, and petroligenic natural gas. Argon is more soluble in water than nitrogen is, and therefore the gases dissolved in mineral springs may be higher in argon than the air is. According to the analyses collected and published by Sborgi (1942), mineral-spring gases contain up to 1.7 per cent A by volume, and the mine gases from the Stassfurt area in Germany may run as high as 16.2 per cent—an exceptionally high value. The content of argon in volcanic gases and in petroligenic natural gas is very much lower. Allen and Zies (1923) found that argon in volcanic gases may be of atmospheric origin because the A:N ratio in Katmai gases in Alaska is similar to that found in the air. However, they also considered that the present-day ratio in the atmosphere might be similar to that existing during the earliest stages of the Earth.

The analyses of Lord Rayleigh (1939) presented in Table 45.3 show that the argon content, like that of neon, in igneous rocks is remarkably constant. Like neon, argon is probably trapped in the structures of minerals.

Argon is the most abundant of the inert gases in the atmosphere. The inert gases afford a good example of the strong individual fluctuations in the abundance from element to element, discussed in chapter 2. The absolute abundance of these gases decreases continuously from helium to xenon by about two powers of 10 (see Fig. 2.2). However, the behavior of argon is completely anomalous. It has three isotopes— A^{36} , A^{38} , and A^{40} —of which the main isotope, A^{40} , is about three hundred times too abundant. The other two isotopes, on the other hand, would agree well with the rule. The explanation of the abnormally high abundance is, according to v. Weizsäcker (1937*a*), that the isotope $^{18}A^{40}$ is formed from its isobar $^{19}K^{40}$, which is radioactive. Thereby the abundance of argon has increased enormously, and v. Weizsäcker considers all atmospheric A^{40} a product of the decay of K^{40} in the lithosphere, but only after the escape of the inert gases from the protoatmosphere. He also attributes the terrestrial deficiency of the inert gases to the fact that they were unable to form stable chemical compounds during the astronomical periods in the Earth's evolution.

The astonishingly high terrestrial abundance of argon may also be explained by the use of Mattauch's rule, as Paneth (1942) has done.

If two neighboring elements in the Periodic System possess isobars, one of the nuclides in question is almost invariably unstable and changes into its isobar by emitting an electron or a positron or both. Consequently, in the case of the isobars $_{13}\text{A}^{40}$, $_{19}\text{K}^{40}$, and $_{20}\text{Ca}^{40}$, $_{19}\text{K}^{40}$ emits β -particles—and thus changes into $_{20}\text{Ca}^{40}$ —and also positrons, thereby producing $_{13}\text{A}^{40}$. According to Suess (1948), only a small percentage of decaying K^{40} is converted into A^{40} , viz., more than 0.5 per cent and less than 10 per cent. The major part of the A^{40} formed is probably left occluded in the upper lithosphere.

Goldschmidt (1937*b*) thought that the low abundance of neon in the Earth's atmosphere, as compared with argon, might possibly be due to the lower cosmic abundance of neon. However, according to Unsöld (1941), the cosmic abundance of neon is rather high. It may be concluded that argon is probably no more abundant cosmically than neon is.

Argon used for industrial purposes is recovered only from air.

KRYPTON

Krypton is found in mineral waters, some volcanic gases, and as a constituent of the atmosphere. However, in the first two sources its content always seems to be lower than in the air. The atmosphere is the only industrial source of krypton.

XENON

Like krypton, xenon is found in gases from mineral springs, from volcanic emanations, and as a constituent of the atmosphere. Its solubility in water is greater than that of any other inert gas, with the exception of radon. It is isolated only from the atmosphere.

SHORT-LIVED RADIOACTIVE AND
ARTIFICIAL ELEMENTS

THE following elements are included in the group of short-lived radioactive and artificial elements: (1) the “missing” elements technetium ($Z = 43$), promethium ($Z = 61$), astatine ($Z = 85$), and francium ($Z = 87$); (2) the short-lived members of the three heavy natural radioactive series, viz., polonium ($Z = 84$), radon ($Z = 86$), radium ($Z = 88$), actinium ($Z = 89$), and protactinium ($Z = 91$); and (3) the transuranium elements neptunium ($Z = 93$), plutonium ($Z = 94$), americium ($Z = 95$), and curium ($Z = 96$).

The common property of all these elements is their radioactivity. They do not possess any stable isotopes, and some of them are known only as products of artificial atomic transmutation. Geochemically, such of these elements as are found in Nature are characterized by a very low abundance. The general rule, valid for the occurrence of the radioactive elements in Nature, is that only such nuclides are present which have half-lives of the same degree of magnitude as the length of the geological evolution of the Earth. Moreover, other elements may be present which are formed as disintegration products of longer-lived nuclides.

Terrestrial abundance values are known only for polonium, radium, actinium, and protactinium. They are calculated from the uranium content of the material analyzed by applying the principles of radioactive equilibrium.

Polonium, radon, radium, actinium, and protactinium are absent in the Sun's atmosphere, and the presence of the other elements discussed in this chapter is still unsettled.

With reference to their general geochemical character, the short-lived members of the natural radioactive series are pronouncedly lithophile, with the exception of radon, which is atmophile. The transuranium elements evidently are also lithophile.

SHORT-LIVED RADIOACTIVE AND ARTIFICIAL ELEMENTS

THE "MISSING" ELEMENTS

The elements included in this group fill the four positions in the Periodic System which remained vacant for a long time, and, in spite of several claims, no conclusive proof has ever been presented of the existence of these elements in Nature.

Seaborg (1948), when discussing the possible occurrence of technetium, promethium, astatine, and francium in Nature concludes, on theoretical grounds, that all the isotopes of these elements should be unstable. Astatine and francium are represented only by radioactive isotopes of too short half-life to allow their presence in weighable amounts in Nature. In the case of technetium and promethium the theoretical deductions are less conclusive. Because stable isotopes of elements with odd atomic number have odd mass number, the stable isotopes of technetium, if they exist, must have the mass numbers 95, 97, and 99, and the stable isotopes of promethium the mass numbers 145, 147, and 149. However, Mattauch's rule (see chap. 2) states that stable isobars of neighboring elements do not exist. Provided that this rule is valid in the region of technetium and promethium in the Periodic System, molybdenum ($Z = 42$) and ruthenium ($Z = 44$) already include among their stable isotopes the mass numbers 95, 97, and 99, and neodymium ($Z = 60$) and samarium ($Z = 62$) the mass numbers 145, 147, and 149. Therefore, the conclusion follows that all isotopes of technetium and promethium are radioactive, and it is likely that they do not exist in megascopic amounts in Nature. However, the possibility is not wholly excluded that radioactive isotopes exist which have sufficiently long half-lives or have proper genetic relationships with neighboring elements to be present in detectable quantities in Nature.

TECHNETIUM

Technetium now occupies the place in the Periodic System formerly held by masurium. The technetium isotopes Tc^{95} and Tc^{97} are produced from molybdenum by bombardment by neutrons or deuterons. The isotope Tc^{99} is obtained among the fission products of uranium. A number of other isotopes, all unstable, are known in addition. The negative β -particle-emitting isotope Tc^{99} has a half-life of $1 \cdot 10^6$ years. It is the stablest of the technetium isotopes. None of the technetium isotopes has been reported to occur in Nature, but, owing to the long half-life, it might be possible that traces of Tc^{99} actually oc-

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cur among the products of the natural fission of uranium which is caused by the action of neutrons of various origin.

In its chemical properties, technetium resembles rhenium rather closely and to a much greater extent than it resembles manganese.

PROMETHIUM

Promethium is a member of the lanthanide group. The isotopes Pm^{147} , Pm^{148} , Pm^{149} , and Pm^{153} are known with definite certainty. The isotope Pm^{147} has the highest half-life (3.7 years). Some of the promethium isotopes are produced by the irradiation of praseodymium and neodymium by helium ions, neutrons, and deuterons. The isotopes Pm^{147} and Pm^{149} are produced in the neutron-induced fission of uranium. The presence of promethium (illinium, florentium) in Nature has been claimed by earlier investigators, but no convincing evidence has ever been presented, and it is very likely that such information is erroneous. Exhaustive research for promethium in Nature has yielded negative results. Ballou (1948) concludes that if promethium does exist in Nature, it is probably the isotope of the mass 145. He suggests the possibility that Nd^{145} is β -active and forms Pm^{145} , which may be a fairly long-lived α -emitter—a fact which explains the very low abundance or nonexistence of promethium in Nature.

Chemically, promethium behaves much like neodymium.

ASTATINE

Astatine is the only halogen which does not possess stable isotopes. The radioactive isotope At^{211} has been produced by bombarding bismuth with α -particles in the cyclotron. Karlik and Bernert (1944) claimed that very short-lived radioactive isotopes of astatine, viz., At^{215} , At^{216} , and At^{218} , formed from the α -emitters AcA, ThA, and RaA (Ac, Th, and Ra emanations), occur in all three natural heavy radioactive series. However, their evidence with reference to At^{215} still remains to be confirmed, but the other two astatine isotopes evidently are to be considered to occur in Nature. Along with At^{211} , At^{217} has also been artificially produced.

The general chemical behavior of astatine is that of a metal, and it shows little resemblance to the other halogens, being more electropositive in character than the other elements in this subgroup. Its chemical properties resemble the properties of polonium very closely, and it is, at any rate, closer to polonium than to iodine.

SHORT-LIVED RADIOACTIVE AND ARTIFICIAL ELEMENTS

In higher animals, astatine concentrates in the thyroid gland like iodine.

FRANCIUM

A naturally radioactive isotope of francium, Fr^{223} , first named AcK, was discovered by Perey (1939) in the actinium family. It is formed from Ac^{227} by α -particle emission and has a half-life of 21 minutes. Another isotope of francium, Fr^{221} , is a member of the synthetic radioactive neptunium series. According to Seaborg (1948), the isotope Fr^{223} may also be readily obtained from uranium piles.

Francium has the chemical properties of an alkali metal.

THE SHORT-LIVED MEMBERS OF THE THREE NATURAL RADIOACTIVE SERIES

Three natural radioactive series are known—the thorium series, the uranium-radium series, and the actinium series. These series are often called the $4n$, the $4n + 2$, and the $4n + 3$ series, respectively, according to the general formula of the mass numbers of the member nuclides. The artificial $4n + 1$ series is also known; it is called the neptunium series, according to Np^{237} , the long-lived parent-isotope. Moreover, an artificial branch of the U-Ra series is known, called the protactinium series after Pa^{230} , which is its first member. The protactinium isotopes Pa^{227} and Pa^{228} are the parent-elements in the artificial collateral branches of the actinium and thorium series, respectively, but it is possible that progenitors with a higher atomic number exist in these collateral series (Ghiorso, Meinke, and Seaborg, 1948).

Polonium, radon, radium, actinium, and protactinium are members of the three natural radioactive series. Consequently, they result partly from the radioactive decay of uranium and partly from the decay of thorium. Therefore, all these elements follow uranium and thorium in the meteorite phases and in igneous rocks. Geochemically, thorium and uranium are pronouncedly lithophile elements, which become enriched in silicate meteorites and in igneous rocks of the upper lithosphere. Like thorium and uranium, the radioactive elements discussed are strongly enriched during the last stages of magmatic crystallization, and their highest concentration takes place in pegmatites and in pneumatolytic and hydrothermal rocks which are rich in thorium and uranium.

In igneous rocks the main seats of radioactivity are the micas muscovite and biotite, zircon, allanite, and sphene. Somewhat less radio-

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activity is attributed to magnetite, apatite, and rutile. According to Goodman and Evans (1941), the radioactivity of the ferromagnesium minerals, in general, is higher than the radioactivity of the salic constituents. The higher activity may be due to inclusions of zircon, allanite, and sphene. Hutton (1947) found that zircon in some granites is not radioactive, whereas monazite and xenotime in the same rocks are strongly radioactive. The radioactivity of zircon is due to small amounts of thorium diadochically replacing zirconium in the structure.

R. J. Strutt (Lord Rayleigh) observed, in 1905, that the radioactivity of igneous rocks increases with their silica content. It has also been reported that radioactivity increases with the content of potas-

TABLE 46.1
ABUNDANCE OF POLONIUM, RADIUM, ACTINIUM, AND PROTACTINIUM

MATERIAL	Po	Ra	Ac	Pa
	g/ton			
Meteoritic iron	$0.00001 \cdot 10^{-6}$	$0.03 \cdot 10^{-6}$	$0.00001 \cdot 10^{-6}$	$0.02 \cdot 10^{-6}$
Silicate meteorites	$0.00003 \cdot 10^{-6}$	$0.12 \cdot 10^{-6}$	$0.00003 \cdot 10^{-6}$	$0.08 \cdot 10^{-6}$
Igneous rocks	$0.0003 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	$0.0003 \cdot 10^{-6}$	$0.8 \cdot 10^{-6}$

sium. However, Barth (1938) found no correlation between radioactivity and the content of FeO and K₂O in Finnish granites, but a correlation was present between radioactivity and the content of biotite.

In sediments and their derivatives the principal loci of radioactivity are the heavy minerals of sands and sandstones, potassium-bearing micas and their alteration products and other potassium-bearing minerals, evaporates, brines connected with petroleum, and sediments of colloidal deposition (Beers and Goodman, 1944). The content of organic matter in shales correlates with the content of uranium and thorium. According to Beers (1945), black shales rich in organic matter are strongly radioactive, and excellent correlation exists between the uranium content, the Th:U ratio, and the carbon content of shales.

The amount of radioactive matter in the Earth's crust is steadily decreasing. If the length of the geological evolution of the Earth is assumed to be $2,000 \cdot 10^6$ years, the content of uranium has decreased by 23 per cent, that of thorium by 7.5 per cent, that of actinium by

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more than 99 per cent, and that of the radioactive potassium isotope K^{40} by 64 per cent (Miholić, 1947).

The abundance of polonium, radium, actinium, and protactinium is presented in Table 46.1. The values are those given by Goldschmidt (1937*b*), with the exception of the actinium content of igneous rocks, which is the value presented by Hevesy (1932). The uranium abundance 4 g/ton in igneous rocks is the basis of the calculations. Radium is the most abundant among the elements listed in Table 46.1.

POLONIUM

Naturally radioactive isotopes of polonium occur in all the three heavy radioactive series. Artificial isotopes are known, in addition. Polonium occurs in all uranium minerals. The longest-lived of the natural isotopes is Po^{210} (RaF), with a half-life of 140 days. The existence of an artificial isotope, Po^{208} , with a half-life of 3 years is probable.

RADON

The isotope Rn^{222} is the immediate result of the radioactive decay of radium. It has a half-life of nearly 4 days. It is usually mixed with its short-lived isotopes Rn^{219} or actinon (An) and Rn^{220} or thoron (Tn), which are produced in the decay of the radium isotopes belonging to the actinium and thorium families.

Radon has the properties of an inert gas. It is typically atmophile and escapes from rocks into the atmosphere or is dissolved in ground water and in thermal waters. In addition, radon tends to concentrate in petroleum and is the most important of the radioactive elements found therein. Most of the radium contained in petroleum has been dissolved from the surrounding sedimentary rocks.

The content of radon in dry air is $4.52 \cdot 10^{-17}$ per cent by weight.

RADIUM

Radium is the most important short-lived natural radioactive element. Four natural radioactive isotopes are known, viz., Ra^{223} (AcX), Ra^{224} (ThX), Ra^{226} , and Ra^{228} (MsTh₁). The Ra^{226} isotope has the highest half-life, viz., 1,590 years. The isotope Ra^{225} is artificial.

The accompanying table gives the average radium content in the various groups of the igneous rocks.

A comparison with Table 46.1 shows that the radium content in stony meteorites is a little less than that in basic igneous rocks.

During weathering, the radioactive elements may become sepa-

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rated from their parent-elements as a result of the differences in their chemical behavior. Therefore, radium, which resembles the alkaline-earth metals chemically, is partly transported into the ocean. A little radium is present in sea water, but, in general, radium is strongly depleted therein. The explanation of the conspicuous lack of radium compared with the considerably higher content of uranium is that the bulk of thorium—among others, the isotope Th^{230} , or ionium, which is the immediate parent of radium—is precipitated by adsorption on ferric and manganic hydroxide. Thus the bulk of ionium formed from uranium is removed from solution, and only the small part which remains decays to produce radium (Föyn, Karlik, Pettersson, and Rona, 1939; Pettersson, 1939). According to Piggot and Urry (1941), the precipitation of uranium is, furthermore, prevented by the carbonate ions present in solution. It has also been claimed that radium

Material	Ra (g/ton)
Ultrabasic igneous rocks (calculated from Davis, 1947).....	0 009·10 ⁻⁶
Basic igneous rocks (Evans, Goodman, and Keevil, 1942).....	0.6·10 ⁻⁶
Intermediate igneous rocks (Senftle and Keevil, 1947).....	0 917·10 ⁻⁶
Granitic rocks (Senftle and Keevil, 1947).....	1 395·10 ⁻⁶

is removed from the sea by chemical and biological extraction in the surface layer, e.g., by incorporation into calcareous structures; but these processes, according to Föyn, Karlik, Pettersson, and Rona, are of minor importance. However, because the solubility of radium carbonate is much lower than the solubility of calcium carbonate, it might be possible that a slight increase in the Ra:Ca ratio takes place during the biological extraction of the two metals from sea water. Moreover, submarine volcanic activity may release hydrochloric acid, which dissolves calcium from the calcareous shells and therefore causes a selective enrichment of radium. Consequently, it is likely that the abyssal radium is partly igneous, partly biological in origin.

It is generally claimed that the deep-sea sediments are particularly rich in radium. However, Pettersson (1943) pointed out that the red clay and the *Globigerina* ooze are not higher in radium than the more active granites are. On the other hand, the manganese nodules, like the manganese-rich lake and bog iron ores, are rich in radium and may contain as much as $135 \cdot 10^{-6}$ g/ton Ra in their surface layer.

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According to Pettersson, there is a very sharp decline of the radium content in the inner layers of the nodules, caused by the fact that radium, unsupported by its parent-element ionium, has accompanied manganese in the nodules. Both manganese and radium come from the red clay which represents the remains of the *Globigerina* ooze after the dissolution of calcium carbonate. The average radium content of sedimentary rocks is given in the accompanying table.

Material	Ra (g./ton)
Sandstones (Bell, Goodman, and Whitehead, 1940).	$0.71 \cdot 10^{-6}$
Shales (Bell, Goodman, and Whitehead, 1940).....	$1.08 \cdot 10^{-6}$
Limestones (Evans and Goodman, 1941).....	$0.42 \cdot 10^{-6}$

According to Beers and Goodman (1944), quartz sands and limestones often contain less than $0.1 \cdot 10^{-6}$ g/ton Ra. In the resistates the average radium content is lower than the average for all igneous rocks. On an average, the limestones are lower in radium than the sandstones are, but their radium content is more constant than the content in sandstones. Limestones containing admixed argillaceous material are higher in radium than are pure limestones. In shales the radium content is fairly constant.

The content of radium is low in crude oil but high in the brines associated with petroleum. According to Bell, Goodman, and Whitehead (1940), the average radium content of crude oil is $0.018 \cdot 10^{-6}$ g/ton Ra. Some of the radium in the brines is the result of leaching from surrounding rocks and from source sediments, but another part is due to the content of radioactive elements in the organic matter converted into petroleum. Radium is enriched in phytoplankton and in many other aqueous organisms. In living diatoms the radium content may be one thousand times as high as in sea water. However, the biological role of radium, if any, is still unknown.

Radium is present in many mineral waters, which have extracted it from the surrounding rocks.

The radium ores are the same as the uranium ores (see chap. 30). Uraninite, first mined at Jáchymov (Joachimstal) in Czechoslovakia, is the principal ore mineral of radium. The largest deposits are found in the vicinity of the Great Bear Lake in Canada.

ACTINIUM

The isotopes Ac^{227} and Ac^{228} are naturally radioactive. The half-life of Ac^{227} is 13.5 years. The isotope Ac^{225} has been prepared artificially.

Actinium is found in all uranium ores but always in very low con-

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centrations. It shows considerable chemical similarity with the lanthanides. The actinide series of elements, similar to the lanthanide series, will be discussed under the transuranium elements.

PROTACTINIUM

Protactinium is the immediate parent of actinium. Two naturally radioactive isotopes are known, viz., Pa^{231} , with a half-life of $3.2 \cdot 10^4$ years, and Pa^{234} . The isotope Pa^{233} has been artificially prepared. Chemically, protactinium resembles thorium, zirconium, and hafnium.

Evans, Hastings, and Schumb (1939) found $0.46 \cdot 10^{-6}$ g/ton Pa in a granite and $0.035 \cdot 10^{-6}$ g/ton in a stony meteorite.

THE TRANSURANIUM ELEMENTS

Sir John Cockcroft and E. Walton in 1931 were the first to accomplish an artificial nuclear disintegration. More than 450 induced radioactivities are now known, and every element in the Periodic System of atomic number from 1 to 96, inclusive, has at least one radioactive isotope. They include the transuranium elements, of which four, viz., neptunium, plutonium, americium, and curium, are already known. All the transuranium elements are artificially produced from uranium, either directly or indirectly.

The existence of a series of transuranium elements was predicted by Niels Bohr as early as 1922 from theoretical considerations. Goldschmidt (1937c), in a theoretical discussion on the different possibilities of the existence of a transuranium series of elements, considered a series of quadripositive thorides following thorium more probable than a series of tripositive actinides following actinium. However, according to Zachariasen (1948), there actually exist two prominent valence states of the heavy elements. Actinium, uranium, neptunium, plutonium, and americium form tripositive ions; and thorium, protactinium, uranium, neptunium, plutonium, and americium form quadripositive ions. Therefore, one should speak of a series of trivalent actinides and of another series of quadrivalent thorides. The continual decrease in the ionic size of these metals, predicted by Goldschmidt (1937c), is actually observed, according to Zachariasen, and the actinide and thoride contractions are analogous to the lanthanide contraction of the rare-earth elements. Goldschmidt, further, suggested that the actinides might occur in Nature in the company of the cerium-earth metals, particularly with neodymium and samarium, owing to the similarity of the ionic size. The thorides, on the

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other hand, would be present in minerals of quadrivalent thorium and uranium, and the higher members of the series would occur in zirconium minerals or in minerals containing quadrivalent cerium. Still another possibility would be the capture of the thorides in the yttrium-earth minerals, in which thorium is known to become concentrated, and in calcium minerals. As a matter of fact, quadrivalent thorium and uranium occur in some fluorites. Goldschmidt (1942) saw no support for the assumption that elements with atomic number higher than 92 should have too short half-lives to allow their presence in Nature.

The metals following actinium in the Periodic System form a transition series of elements in which the inner $5f$ electron shell is being filled in a similar manner as the inner $4f$ shell in the lanthanide series (see chap. 18). Chemically, many of the members of this succession of elements resemble the lanthanides rather closely. Thus, for instance, americium and curium are quantitatively carried by the lanthanide fluorides and are separated from the lanthanides only with difficulty.

It is possible that other transuranium elements which have atomic numbers greater than 96 may be artificially produced. According to Seaborg (1948), it is probable that the longest-lived isotopes of the elements 97 and 98 will have mass numbers as high as 247 and 248, and still higher.

NEPTUNIUM

Neptunium was the first transuranium element to be discovered. Irradiation of uranium by neutrons leads to the production of the isotope Np^{239} from U^{239} , its immediate parent. Another isotope, Np^{237} , is produced by bombarding uranium with fast neutrons and is a result of decay of U^{237} . The half-life of Np^{237} , the longest-lived isotope, is $2.25 \cdot 10^6$ years. Four other neptunium isotopes are known, in addition.

According to Seaborg (1945), there will be some neptunium in the upper lithosphere, but its content will be less than that of plutonium. It is formed from uranium by the action of neutrons of various origin.

Neptunium is similar in chemical properties to uranium.

PLUTONIUM

The second transuranium element discovered was plutonium. Its first-discovered isotope is Pu^{238} , which has a half-life of 50 years and results from U^{238} by deuteron bombardment. The isotope Pu^{239} , with

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a half-life of 24,100 years, is a decay product of Np^{239} . It is the most important among the plutonium isotopes because it undergoes fission when bombarded with slow neutrons. It is now being produced in industrial amounts. The isotope Pu^{241} is also known; it has a long half-life.

Goldschmidt (1942) predicted the presence of plutonium in beryllium-bearing uranium minerals as a result of neutron bombardment. The prediction was fulfilled when very small amounts of plutonium were found in pitchblende of the Great Bear Lake region in Canada and in carnotite (Seaborg and Perlman, 1948; Seaborg, 1948). The upper limit of the plutonium content is 0.001–0.01 g/ton, and the most probable value, for Pu^{239} , is 10^{-9} g/ton. According to Seaborg and Segrè (1947), Pu^{239} is present in pitchblende, in spite of its relatively short half-life, probably because it is continually formed by the absorption in U^{238} of neutrons from various sources. Neutrons are always available for this purpose.

The chemical properties of plutonium resemble those of uranium and neptunium. The first pure compound of plutonium was prepared by B. B. Cunningham and L. B. Werner in the United States in 1942. That year, therefore, marks the first isolation of a compound of an artificially produced isotope of any element.

AMERICIUM

Americium was the fourth transuranium element which was discovered. The isotope Am^{241} results from the bombardment of U^{238} with very high-energy helium ions. The plutonium isotope Pu^{241} is formed first, and it decays into Am^{241} . The half-life of Am^{241} is 500 years. The short-lived (18 hours) isotope Am^{242} is also known.

Seaborg (1945) concludes that some americium and curium are present in the Earth's crust but that their content is still lower than the content of neptunium. According to Seaborg and Segrè (1947), they are formed from uranium by neutrons of various origin.

CURIUM

Curium was the third transuranium element to be discovered. The isotope Cm^{242} is formed by α -particle bombardment from Pu^{239} or by neutron irradiation from Am^{241} . Its half-life is 150 days. The half-life of the other known isotope of curium, Cm^{240} , is 30 days.

The occurrence of curium in Nature was discussed under americium.

APPENDIXES

(a) THE PERIODIC SYSTEM

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(b) THE PERIODIC TABLE

PERIODS ↓	GROUPS →	I	II	III	IV	V	VI	VII	VIII		PERIODS ↓	
1	0 n	1 H								2 He		1
2	2 He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne		2	
3	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		3	
4	18 Ar	19 K 29 Cu	20 Ca 30 Zn	21 Sc 31 Ga	22 Ti 32 Ge	23 V 33 As	24 Cr 34 Se	25 Mn 35 Br	36 Kr	26 Fe 27 Co 28 Ni	4	
5	36 Kr	37 Rb 47 Ag	38 Sr 48 Cd	39 Y 49 In	40 Zr 50 Sn	41 Nb 51 Sb	42 Mo 52 Te	43 Tc 53 I	54 Xe	44 Ru 45 Rh 46 Pd	5	
6	54 Xe	55 Cs 79 Au	56 Ba 80 Hg	57 La • 81 Tl	72 Hf 82 Pb	73 Ta 83 Bi	74 W 84 Po	75 Re 85 At	86 Rn	76 Os 77 Ir 78 Pt	6	
7	86 Rn	87 Fr	88 Ra	89 Ac ••								

6	• 58-71 The lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	6
7	•• 90-96 The actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm								7

APPENDIX 2

ATOMIC WEIGHTS FOR 1948

O = 16 0000

Z	Element	Symbol	Atomic Weight
13.. . . .	Aluminum	Al	26 97
51	Antimony	Sb	121.76
18	Argon	A	39 944
33.. . . .	Arsenic	As	74 91
56.. . . .	Barium	Ba	137 36
4.	Beryllium	Be	9 02
83.	Bismuth	Bi	209 00
5	Boron	B	10 82
35.	Bromine	Br	79 916
48.	Cadmium	Cd	112 41
20.	Calcium	Ca	40 08
6.	Carbon	C	12 010
58.. . . .	Cerium	Ce	140 13
55.. . . .	Cesium	Cs	132 91
17	Chlorine	Cl	35 457
24	Chromium	Cr	52 01
27.	Cobalt	Co	58 94
41	Columbium	Cb	92 91
29	Copper	Cu	63 54
66.	Dysprosium	Dy	162 46
68.. . . .	Erbium	Er	167 2
63.. . . .	Europium	Eu	152.0
9.....	Fluorine	F	19 00
64.	Gadolinium	Gd	156 9
31.. . . .	Gallium	Ga	69.72
32.	Germanium	Ge	72 60
79.	Gold	Au	197 2
72.. . . .	Hafnium	Hf	178 6
2.	Helium	He	4 003
67.	Holmium	Ho	164.94
1	Hydrogen	H	1.0080
49.	Indium	In	114.76
53.. . . .	Iodine	I	126.92
77.. . . .	Iridium	Ir	193.1
26.. . . .	Iron	Fe	55 85
36.....	Krypton	Kr	83.7
57.. . . .	Lanthanum	La	138 92

APPENDIX 2—Continued

Z	Element	Symbol	Atomic Weight
82	Lead	Pb	207.21
3	Lithium	Li	6.940
71	Lutecium	Lu	174.99
12	Magnesium	Mg	24.32
25	Manganese	Mn	54.93
80	Mercury	Hg	200.61
42	Molybdenum	Mo	95.95
60	Neodymium	Nd	144.27
10	Neon	Ne	20.183
28	Nickel	Ni	58.69
7	Nitrogen	N	14.008
76	Osmium	Os	190.2
8	Oxygen	O	16.0000
46	Palladium	Pd	106.7
15	Phosphorus	P	30.98
78	Platinum	Pt	195.23
19	Potassium	K	39.096
59	Praseodymium	Pr	140.92
91	Protactinium	Pa	231
88	Radium	Ra	226.05
86	Radon	Rn	222
75	Rhenium	Re	186.31
45	Rhodium	Rh	102.91
37	Rubidium	Rb	85.48
44	Ruthenium	Ru	101.7
62	Samarium	Sm	150.43
21	Scandium	Sc	45.10
34	Selenium	Se	78.96
14	Silicon	Si	28.06
47	Silver	Ag	107.880
11	Sodium	Na	22.997
38	Strontium	Sr	87.63
16	Sulfur	S	32.066
73	Tantalum	Ta	180.88
52	Tellurium	Te	127.61
65	Terbium	Tb	159.2
81	Thallium	Tl	204.39
90	Thorium	Th	232.12
69	Thulium	Tm	169.4
50	Tin	Sn	118.70
22	Titanium	Ti	47.90
74	Tungsten	W	183.92
92	Uranium	U	238.07
23	Vanadium	V	50.95
54	Xenon	Xe	131.3
70	Ytterbium	Yb	173.04
39	Yttrium	Y	88.92
30	Zinc	Zn	65.38
40	Zirconium	Zr	91.22

APPENDIX 3

ATOMIC AND IONIC RADII OF THE ELEMENTS

The atomic radii are half the closest approach of the atoms. The ionic radii are those for 6-fold co-ordination. All values are given in kX.

(0.47): theoretical value; [1.00]: value based on a radius of 1.40 kX for O^{2-}

A	1 91	Cb	1.43	Fa		Li	1.52
Ac		Cb ⁴⁺	0 69	Fe	1.24	Li ⁺	0.78
Ac ³⁺	[1.11]	Cb ⁵⁺	0.69	Fe ²⁺	0.83	Lu	1.74
Ag	1.44			Fe ³⁺	0 67	Lu ³⁺	0.99
Ag ⁺	1.13	Cd	1 49	Ga	1.22	Mg	1.60
Al	1 43	Cd ²⁺	1 03	Ga ³⁺	0 62	Mg ²⁺	0.78
Al ³⁺	0 57	Ce	1 82	Gd	1.79	Mn	1.18
Am		Ce ³⁺	1.18 [1.02]	Gd ³⁺	1.11	Mn ²⁺	0.91
Am ³⁺	[1 00]	Ce ⁴⁺	1 02	Ge	1.22	Mn ³⁺	0.70
Am ⁴⁺	[0.85]	Cl ⁻	1 81	Ge ⁴⁺	0.44	Mn ⁴⁺	0.52
As	1 25	Cl	1.07	H ⁻	1.54	Mn ⁷⁺	0 35
As ³⁺	0 69	Cl ⁷⁺	(0.26)	H	0.46	Mo	1.36
As ⁵⁺	0 47	Cm		He	1 45	Mo ⁴⁺	0 68
At		Co	1.25			Mo ⁶⁺	(0 62)
Au	1 44	Co ²⁺	0 82	Hf	1 58	N	0.71
Au ⁺	(1 37)	Co ³⁺	0.65	Hf ⁴⁺	0 86	N ⁶⁺	0.15
B	0 97	Cr	1.25	Hg	1.50	Na	1.86
B ³⁺	(0 20)	Cr ³⁺	0 64	Hg ²⁺	1.12	Na ⁺	0 98
Ba	2 17	Cr ⁶⁺	0 35	Ho	1 76	Nd	1.82
Ba ²⁺	1 43	Cs	2.62	Ho ³⁺	1.05	Nd ³⁺	1.15 [0.99]
Be	1 12	Cs ⁺	1 65	I ⁻	2 20	Ne	1.60
Be ²⁺	0.34	Cu	1 28	I	1 36	[NH ₄] ⁺	1 43
Bi	1 55	Cu ⁺	(0 96)	I ⁵⁺	0 94	Ni	1.24
Bi ³⁺	1 20	Cu ²⁺	~0 83	I ⁷⁺	(0 50)	Ni ²⁺	0.78
Bi ⁵⁺	(0.74)	Dy	1 77	In	1 62	Np	
Br ⁻	1 96	Dy ³⁺	1 07	In ³⁺	0.92	Np ³⁺	[1.02]
Br	1 19	Er	1.75	Ir	1.35	Np ⁴⁺	[0.88]
Br ⁷⁺	(0 39)	Er ³⁺	1 04	Ir ⁴⁺	0.66	O ²⁻	1.32
C	0 77	Eu	2.04	K	2.31	O	0.60
C ⁴⁺	(0 15)	Eu ²⁺	1 24	K ⁺	1.33	[OH] ⁻	1.33
Ca	1 96	Eu ³⁺	1 13 [0.97]	Kr	2 01	Os	1 35
Ca ²⁺	1 06	F ⁻	1 33	La	1.87	Os ⁴⁺	0.67
		F		La ³⁺	1 22 [1.04]		

APPENDIX 3—Continued

P		Re	1.38	Sn ⁴⁻	2.15	U	1.38
P ⁶⁺	0.35	Re ⁴⁺	0.56	Sn	1.40	U ³⁺	[1.04]
Pa				Sn ⁴⁺	0.74	U ⁴⁺	1.05[0.89]
Pa ³⁺	[1.06]	Rh	1.34			V	1.30
Pa ⁴⁺	[(0.91)]	Rh ³⁺	0.68	Sr	2.15	V ³⁺	0.65
Pb ⁴⁻	2.15	Rn		Sr ²⁺	1.27	V ⁴⁺	0.61
Pb	1.75			Ta	1.43	V ⁵⁺	~0.4
Pb ²⁺	1.32	Ru	1.33	Ta ⁵⁺	0.68	W	1.36
Pb ⁴⁺	0.84	Ru ⁴⁺	0.65			W ⁴⁺	0.68
Pd	1.97	S ²⁻	1.74	Tb	1.77		
Pd ⁴⁺	0.50	S	1.04	Tb ³⁺	1.09	Xe	2.20
Pm		S ⁶⁺	0.34	Tc		Y	1.81
Pm ³⁺	[(0.98)]	Sb	1.45	Te ²⁻	2.11	Y ³⁺	1.06
Po	1.41	Sb ³⁺	0.90	Te	1.43	Yb	1.93
Pr	1.82	Sb ⁵⁺	(0.62)	Te ⁴⁺	0.89	Yb ²⁺	1.03
Pr ³⁺	1.16[1.00]			Te ⁶⁺	(0.56)	Yb ³⁺	1.00
Pr ⁴⁺	1.00	Sc	1.51	Th	1.80	Zn	1.33
Pt	1.38	Sc ³⁺	0.83	Th ³⁺	[1.08]	Zn ²⁺	0.83
Pt ⁴⁺	0.52	Se ²⁻	1.91	Th ⁴⁺	1.10[0.95]	Zr	1.56
Pu		Se	1.16	Ti	1.46	Zr ⁴⁺	0.87
Pu ³⁺	[1.01]	Se ⁶⁺	0.3-0.4	Ti ³⁺	0.69		
Pu ⁴⁺	[0.86]	Si ⁴⁻	1.98	Ti ⁴⁺	0.64		
Ra		Si	1.17	Tl	1.70		
Ra ²⁺	1.52	Si ⁴⁺	0.39	Tl ⁺	1.49		
Rb	2.43	Sm	~1.85	Tl ³⁺	1.05		
Rb ⁺	1.49	Sm ³⁺	1.13[0.97]	Tm	1.74		
				Tm ³⁺	1.04		

APPENDIX 4

THE ELECTRONIC STRUCTURE OF THE ELEMENTS

PERI- OD	ATOM- IC NUM- BER	SHELL →	K			L			M			N				O					P			Q				
		Quant- um Group →	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	7s							
		Ele- ment	Number of Electrons in Each Quantum Group																									
I	0	n	0																									
	1	H	1																									
	2	He	2																									
II	3	Li	2																									
	4	Be	2	1																								
	5	B	2	2	1																							
	6	C	2	2	2																							
	7	N	2	2	2	1																						
	8	O	2	2	2	2																						
	9	F	2	2	2	2	1																					
	10	Ne	2	2	2	2	2																					
III	11	Na	filled			1																						
	12	Mg				2																						
	13	Al				2	1																					
	14	Si				2	2																					
	15	P				2	2	1																				
	16	S				2	2	2																				
	17	Cl				2	2	2	1																			
	18	A				2	2	2	2																			
IV	19	K	filled						1																			
	20	Ca							2																			
	21	Sc							2	1																		
	22	Ti							2	2																		
	23	V							3	2																		
	24	Cr							5	1																		
	25	Mn							5	2																		
	26	Fe							6	2																		
	27	Co							7	2																		
	28	Ni							8	2																		
	29	Cu							10	1																		
	30	Zn								2																		
	31	Ga							filled				1															
	32	Ge											2															
	33	As											3															
	34	Se											4															
	35	Br											5															
	36	Kr											6															
V	37	Rb											filled				1											
	38	Sr															2											
	39	Y															2											
	40	Zr															2											
	41	Nb															1											
	42	Mo															1											
	43	Tc															1											
	44	Ru															1											
	45	Rh															1											
	46	Pd															1											
	47	Ag															2											
	48	Cd											filled				2											
	49	In															2											
	50	Sn															2	1										
	51	Sb															2	2										
	52	Te															2	3										
	53	I															2	4										
	54	Xe															2	5										

APPENDIX 4—Continued

PERI- OD	ATOM- IC NUM- BER	SHELL →	K		L		M			N				O					P			
		Quantum Group →	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	7s	
		Element	Number of Electrons in Each Quantum Group																			
VI	55	Cs											2	6				1				
	56	Ba											2	6				1				
	57	La											2	6				1				
	58	Ce										1	2	6				1				
	59	Pr										2	2	6				1				
	60	Nd										3	2	6				1				
	61	Pm										4	2	6				1				
	62	Sm										5	2	6				1				
	63	Eu										6	2	6				1				
	64	Gd										7	2	6				1				
	65	Tb										8	2	6				1				
	66	Dy										9	2	6				1				
	67	Ho										10	2	6				1				
	68	Er										11	2	6				1				
	69	Tm										12	2	6				1				
	70	Yb										13	2	6				1				
	71	Lu										14	2	6				1				
	72	Hf										filled				2						
	73	Ta										filled				3						
	74	W										filled				4						
	75	Re										filled				5						
	76	Os										filled				6						
	77	Ir										filled				9						
	78	Pt										filled				9						
	79	Au										filled				10						
	80	Hg										filled				filled						
81	Tl																					
82	Pb																					
83	Bi																					
84	Po																					
85	At																					
86	Rn																					
VII	87	Fa																				
	88	Ra																				
	89	Ac																				
	90	Th																				
	91	Pa																				
	92	U																				
	93	Np																				
	94	Pu																				
	95	Am																				
	96	Cm																				

APPENDIX 5

GEODETIC AND OTHER TERRESTRIAL DATA

Equatorial radius of the Earth (Birch, Schairer, and Spicer, 1942)	6,378.388 km
Polar radius of the Earth (Birch, Schairer, and Spicer, 1942)	6,356.912 km
Average radius of the Earth (Birch, Schairer, and Spicer, 1942)	$6.371 \cdot 10^8 \text{ cm} = 6,371 \text{ km}$
Volume of the Earth (Birch, Schairer, and Spicer, 1942)	$1.083 \cdot 10^{27} \text{ cm}^3 = 1.083 \cdot 10^{12} \text{ km}^3$
Average density of the Earth (Birch, Schairer, and Spicer, 1942)	$5.517 \text{ g} \cdot \text{cm}^{-3}$
Mass of the Earth (Birch, Schairer, and Spicer, 1942)	$5.977 \cdot 10^{27} \text{ g} = 5.977 \cdot 10^{21} \text{ tons} = 5.977 \cdot 10^7 \text{ Gg}$
Average density of the upper lithosphere (Basement Complex in Finland) (R. A. Daly in Birch, Schairer, and Spicer, 1942)	$2.705 \text{ g} \cdot \text{cm}^{-3}$
Area of surface of the Earth (Birch, Schairer, and Spicer, 1942)	$5.101 \cdot 10^{18} \text{ cm}^2 = 510.1 \cdot 10^6 \text{ km}^2$
Area of surface of dry land (Kossinna, 1921) ..	$148.892 \cdot 10^6 \text{ km}^2$
Area of surface of dry land (Kalle, 1943)	$1.4894 \cdot 10^{18} \text{ cm}^2 = 148.94 \cdot 10^6 \text{ km}^2$
Area of surface of the oceans (Kossinna, 1921) ..	$361.059 \cdot 10^6 \text{ km}^2$
Area of surface of the oceans (Kalle, 1943) ...	$3.6116 \cdot 10^{18} \text{ cm}^2 = 361.16 \cdot 10^6 \text{ km}^2$
Volume of the oceans (Kossinna, 1921)	$1,370.323 \cdot 10^6 \text{ km}^3$
Volume of the oceans (Kalle, 1943)	$1.3722 \cdot 10^{24} \text{ cm}^3 = 1,372.2 \cdot 10^6 \text{ km}^3$
Mass of the oceans (chap. 6)	$14,060 \cdot 10^{20} \text{ g} = 14,060 \text{ Gg}$
Mass of the oceans (Kalle, 1943)	$14,220 \cdot 10^{20} \text{ g} = 1.422 \cdot 10^{18} \text{ tons} \parallel 14,220 \text{ Gg}$
Mass of the atmosphere, minimum (Humphreys, 1940)	$51,300,000 \cdot 10^{11} \text{ kg} = 5.13 \cdot 10^{15} \text{ tons} = 51.3 \text{ Gg}$
Mass of the atmosphere (Kalle, 1943)	$\sim 5.098 \cdot 10^{21} \text{ g} \sim 5.098 \cdot 10^{15} \text{ tons} \sim 50.98 \text{ Gg}$

APPENDIX 6

GRAVIMETRIC CONVERSION FACTORS

Element	Found	Sought	Factor
Aluminum... ..	Al	Al ₂ O ₃	1.88988
	Al ₂ O ₃	Al	0.52913
Antimony... .	Sb	Sb ₂ O ₃	1.19711
	Sb	Sb ₂ O ₅	1.32852
	Sb ₂ O ₃	Sb	0.83535
	Sb ₂ O ₅	Sb	0.75272
Arsenic.... .	As	As ₂ O ₃	1.32038
	As	As ₂ O ₅	1.53400
	As ₂ O ₃	As	0.75736
	As ₂ O ₅	As	0.65190
Barium	Ba	BaO	1.11648
	BaO	Ba	0.89567
Beryllium... .	Be	BeO	2.77384
	BeO	Be	0.36051
Bismuth.	Bi	Bi ₂ O ₃	1.11483
	Bi ₂ O ₃	Bi	0.89700
Boron.	B	B ₂ O ₃	3.21811
	B ₂ O ₃	B	0.31074
Cadmium.	Cd	CdO	1.14234
	CdO	Cd	0.87540
Calcium	Ca	CaO	1.39920
	Ca	CaCO ₃	2.49726
	CaO	Ca	0.71469
	CaO	CaCO ₃	1.78477
	CaCO ₃	Ca	0.40044
	CaCO ₃	CaO	0.56030
Carbon... ..	C	CO ₂	3.66445
	C	CaCO ₃	8.33388
	CO ₂	C	0.27289
	CaCO ₃	C	0.11999
	CaCO ₃	CO ₂	0.43970
Cerium... .	Ce	CeO ₂	1.22836
	Ce	Ce ₂ O ₃	1.17127
	CeO ₂	Ce	0.81409
	CeO ₂	Ce ₂ O ₃	0.95352
	Ce ₂ O ₃	Ce	0.85377
	Ce ₂ O ₃	CeO ₂	1.04874
Cesium.....	Cs	Cs ₂ O	1.06020
	Cs ₂ O	Cs	0.94323
Chlorine	Cl	HCl	1.02843
	HCl	Cl	0.97236
Chromium	Cr	Cr ₂ O ₃	1.46145
	Cr ₂ O ₃	Cr	0.68425
Cobalt.....	Co	CoO	1.27146
	Co	Co ₃ O ₄	1.36195
	CoO	Co	0.78650
	CoO	Co ₃ O ₄	1.07117
	Co ₃ O ₄	Co	0.73424
	Co ₃ O ₄	CoO	0.93356

APPENDIX 6—Continued

Element	Found	Sought	Factor
Columbium..	Cb	Cb ₂ O ₅	1 43052
	Cb ₂ O ₅	Cb	0.69904
Copper . .	Cu	CuO	1 25181
	CuO	Cu	0 79884
Dysprosium	Dy	Dy ₂ O ₃	1 14773
	Dy ₂ O ₃	Dy	0 87129
Erbium..	Er	Er ₂ O ₃	1 14354
	Er ₂ O ₃	Er	0 87448
Europium.	Eu	Eu ₂ O ₃	1 15789
	Eu ₂ O ₃	Eu	0 86364
Fluorine .	F	HF	1 05305
	F	CaF ₂	2 05474
	HF	F	0 94962
	CaF ₂	F	0 48668
Gadolinium . . .	Gd	Gd ₂ O ₃	1. 15296
	Gd ₂ O ₃	Gd	0 86733
Gallium . .	Ga	Ga ₂ O ₃	1 34423
	Ga ₂ O ₃	Ga	0 74392
Germanium. . .	Ge	GeO ₂	1 44077
	GeO ₂	Ge	0.69407
Gold . . .	Au	Au ₂ O	1 04057
	Au	Au ₂ O ₃	1 12170
	Au ₂ O	Au	0 96101
	Au ₂ O	Au ₂ O ₃	1 07797
	Au ₂ O ₃	Au	0 89150
	Au ₂ O ₃	Au ₂ O	0 92767
Hafnium... ..	Hf	HfO ₂	1. 17917
	HfO ₂	Hf	0 84805
Holmium . .	Ho	Ho ₂ O ₃	1 14551
	Ho ₂ O ₃	Ho	0 87298
Hydrogen .	H	H ₂ O	8 93651
	H ₂ O	H	0. 11190
Indium.....	In	In ₂ O ₃	1 20913
	In ₂ O ₃	In	0. 82704
Iridium.....	Ir	IrO ₂	1 16572
	IrO ₂	Ir	0.85784
Iron	Fe	FeO	1. 28648
	Fe	Fe ₂ O ₃	1.42972
	FeO	Fe	0.77731
	FeO	Fe ₂ O ₃	1. 11134
	Fe ₂ O ₃	Fe	0 69944
	Fe ₂ O ₃	FeO	0.89981
Lanthanum ...	La	La ₂ O ₃	1 17276
	La ₂ O ₃	La	0 85269
Lead	Pb	PbO	1 07722
	Pb	PbO ₂	1. 15443
	PbO	Pb	0 92832
	PbO	PbO ₂	1.07168
	PbO ₂	Pb	0 86623
	PbO ₂	PbO	0.93311
Lithium... ..	Li	Li ₂ O	2. 15274
	Li ₂ O	Li	0.46452
Lutecium.....	Lu	Lu ₂ O ₃	1 13715
	Lu ₂ O ₃	Lu	0 87939
Magnesium....	Mg	MgO	1.65789
	MgO	Mg	0.60317
Manganese... ..	Mn	MnO	1.29128
	Mn	MnO ₂	1 53256
	Mn	Mn ₂ O ₃	1 43692
	MnO	Mn	0 77443
	MnO	MnO ₂	1.22557
	MnO	Mn ₂ O ₃	1. 11279

APPENDIX 6—Continued

Element	Found	Sought	Factor
Manganese—Continued	MnO ₂	Mn	0 63189
	MnO ₂	MnO	0 81594
	MnO ₂	Mn ₂ O ₃	0 90797
	Mn ₂ O ₃	Mn	0 69593
	Mn ₂ O ₃	MnO	0 89864
	Mn ₂ O ₃	MnO ₂	1 10186
Mercury . .	Hg	HgO	1 07976
	HgO	Hg	0 92613
	Mo	MoO ₃	1 50026
Molybdenum . .	MoO ₃	Mo	0 66655
	Nd	Nd ₂ O ₃	1 16635
	Nd ₂ O ₃	Nd	0 85737
Neodymium . . .	Ni	NiO	1 27262
	NiO	Ni	0 78578
	N	N ₂ O	1 57110
Nickel	N	N ₂ O ₅	3 85551
	N	NH ₃	1 21588
	N ₂ O	N	0 63650
	N ₂ O ₅	N	0 25937
	NH ₃	N	0 82245
	Os	OsO ₄	1 33649
Osmium	OsO ₄	Os	0 74823
	O	H ₂ O	1 12600
	H ₂ O	O	0 88810
Oxygen	Pd	PdO	1 14995
	PdO	Pd	0 86960
Palladium . . .	P	P ₂ O ₅	2 29116
	P ₂ O ₅	P	0 43646
	Pt	PtO ₂	1 16391
Phosphorus . . .	PtO ₂	Pt	0 85917
	K	K ₂ O	1 20462
	K ₂ O	K	0 83013
Platinum	Pr	Pr ₂ O ₃	1 17031
	Pr ₂ O ₃	Pr	0 85447
	Re	Re ₂ O ₇	1 30057
Potassium . . .	Re ₂ O ₇	Re	0 76889
	Rh	Rh ₂ O ₃	1 23321
	Rh ₂ O ₃	Rh	0 81089
Praseodymium .	Rb	Rb ₂ O	1 09359
	Rb ₂ O	Rb	0 91442
	Ru	RuO ₂	1 31465
Rhenium	RuO ₂	Ru	0 76066
	Sm	Sm ₂ O ₃	1 15954
	Sm ₂ O ₃	Sm	0 86241
Rhodium	Sc	Sc ₂ O ₃	1 53215
	Sc ₂ O ₃	Sc	0 65268
	Se	SeO ₂	1 40527
Rubidium	Se	SeO ₃	1 60790
	SeO ₂	Se	0 71161
	SeO ₂	SeO ₃	1 14420
	SeO ₃	Se	0 62193
	SeO ₃	SeO ₂	0 87398
	Si	SiO ₂	2 14041
	SiO ₂	Si	0 46720
	Ag	Ag ₂ O	1 07416
Ruthenium . . .	Ag ₂ O	Ag	0 93096
	Na	Na ₂ O	1 34787
	Na ₂ O	Na	0 74191
Samarium	Sr	SrO	1 18259
	SrO	Sr	0 84560
Scandium			
Selenium			
Silicon			
Silver			
Sodium			
Strontium			

APPENDIX 6—Continued

Element	Found	Sought	Factor
Sulfur. . . .	S	SO ₂	1 99794
	S	SO ₃	2 49691
	SO ₂	S	0 50052
	SO ₂	SO ₃	1.24974
	SO ₃	S	0 40049
	SO ₃	SO ₂	0.80016
Tantalum..	Ta	Ta ₂ O ₅	1.22114
	Ta ₂ O ₅	Ta	0 81891
Tellurium..	Te	TeO ₂	1.25076
	TeO ₂	Te	0.79951
Terbium...	Tb	Tb ₂ O ₃	1.15075
	Tb ₂ O ₃	Tb	0.86900
Thallium... .	Tl	Tl ₂ O	1.03914
	Tl	Tl ₂ O ₃	1.11742
	Tl ₂ O	Tl	0.96233
	Tl ₂ O	Tl ₂ O ₃	1 07533
	Tl ₂ O ₃	Tl	0 89492
	Tl ₂ O ₃	Tl ₂ O	0.92994
Thorium..	Th	ThO ₂	1 13786
	ThO ₂	Th	0 87884
Thulium..	Tm	Tm ₂ O ₃	1 14168
	Tm ₂ O ₃	Tm	0 87590
Tin.....	Sn	SnO	1.13479
	Sn	SnO ₂	1.26959
	SnO	Sn	0 88122
	SnO	SnO ₂	1.11878
	SnO ₂	Sn	0.78766
	SnO ₂	SnO	0.89383
Titanium....	Ti	TiO ₂	1.66806
	TiO ₂	Ti	0.59950
Tungsten.... .	W	WO ₃	1.26098
	WO ₃	W	0.79303
Uranium.....	U	UO ₂	1.13441
	U	UO ₃	1.20162
	UO ₂	U	0.88151
	UO ₂	UO ₃	1 05924
	UO ₃	U	0.83221
	UO ₃	UO ₂	0 94407
Vanadium... .	V	V ₂ O ₃	1 47105
	V	V ₂ O ₅	1.78508
	V ₂ O ₃	V	0.67979
	V ₂ O ₃	V ₂ O ₅	1.21348
	V ₂ O ₅	V	0.56020
	V ₂ O ₅	V ₂ O ₃	0.82408
Ytterbium.....	Yb	Yb ₂ O ₃	1.13870
	Yb ₂ O ₃	Yb	0.87820
Yttrium.... .	Y	Y ₂ O ₃	1.26991
	Y ₂ O ₃	Y	0.78746
Zinc.....	Zn	ZnO	1.24472
	ZnO	Zn	0 80339
Zirconium.....	Zr	ZrO ₂	1.35080
	ZrO ₂	Zr	0.74030

APPENDIX 7

VARIOUS WAYS OF EXPRESSING CONCENTRATION OR CONTENT, COMMONLY USED IN GEOCHEMICAL CALCULATIONS

COMPARISON OF METRIC MASS UNITS

	γ	mg	g	kg	ton	Gg
γ	1	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-26}
mg	10^3	1	10^{-3}	10^{-6}	10^{-9}	10^{-23}
g	10^6	10^3	1	10^{-3}	10^{-6}	10^{-20}
kg	10^9	10^6	10^3	1	10^{-3}	10^{-17}
ton	10^{12}	10^9	10^6	10^3	1	10^{-14}
Gg	10^{26}	10^{23}	10^{20}	10^{17}	10^{14}	1

SUM OF THE CONSTITUENTS IS 1

CONCENTRATION IN

10^a	g/ton	
10^{-1}	100,000	10^5
10^{-2}	10,000	10^4
10^{-3}	1,000	10^3
10^{-4}	100	10^2
10^{-5}	10	10^1
10^{-6}	1	10^0
10^{-7}	0.1	10^{-1}
10^{-8}	0.01	10^{-2}
10^{-9}	0.001	10^{-3}
10^{-10}	0.0001	10^{-4}
10^{-11}	0.00001	10^{-5}

CONCENTRATION IN

γ/g		$\gamma/100\text{ g}$		γ/kg		g/ton	
1,000	10^3	100,000	10^5	1,000,000	10^6	1,000	10^3
100	10^2	10,000	10^4	100,000	10^5	100	10^2
10	10^1	1,000	10^3	10,000	10^4	10	10^1
1	10^0	100	10^2	1,000	10^3	1	10^0
0.1	10^{-1}	10	10^1	100	10^2	0.1	10^{-1}
0.01	10^{-2}	1	10^0	10	10^1	0.01	10^{-2}
0.001	10^{-3}	0.1	10^{-1}	1	10^0	0.001	10^{-3}
0.0001	10^{-4}	0.01	10^{-2}	0.1	10^{-1}	0.0001	10^{-4}
0.00001	10^{-5}	0.001	10^{-3}	0.01	10^{-2}	0.00001	10^{-5}

CONCENTRATION IN

g/g	g/ton	
10^{-1} ...	100,000	10^5
10^{-2} ...	10,000	10^4
10^{-3} ...	1,000	10^3
10^{-4} ...	100	10^2
10^{-5} ...	10	10^1
10^{-6} ...	1	10^0
10^{-7} ...	0.1	10^{-1}
10^{-8} ...	0.01	10^{-2}
10^{-9} ...	0.001	10^{-3}
10^{-10} ...	0.0001	10^{-4}
10^{-11} ...	0 00001	10^{-5}
10^{-12} ...	0 000001	10^{-6}
10^{-13} ...	0 0000001	10^{-7}
10^{-14} ...	0 00000001	10^{-8}

CONCENTRATION IN

Per Cent		Parts per Thousand		Parts per Million or mg/kg or g/ton	
100	10^2	1,000	10^3	1,000,000	10^6
10	10^1	100	10^2	100,000	10^5
1	10^0	10	10^1	10,000	10^4
0.1	10^{-1}	1	10^0	1,000	10^3
0.01	10^{-2}	0.1	10^{-1}	100	10^2
0.001	10^{-3}	0.01	10^{-2}	10	10^1
0.0001	10^{-4}	0.001	10^{-3}	1	10^0
0.00001	10^{-5}	0.0001	10^{-4}	0.1	10^{-1}
0.000001	10^{-6}	0.00001	10^{-5}	0.01	10^{-2}
0.0000001	10^{-7}	0.000001	10^{-6}	0.001	10^{-3}
0.00000001	10^{-8}	0.0000001	10^{-7}	0.0001	10^{-4}

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